# ENERGY TRANSFER IN MIXTURES OF CARBON DIOXIDE-POLYATOMIC MOLECULES USING LASER INDUCED FLUORESCENCE

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

*by*

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to the

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KANPUR
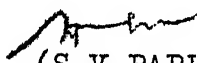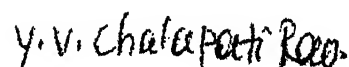
APRIL, 1977

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## CERTIFICATE

This is to certify that the work described in this thesis is the original work of Mr. PALADUGU RAMAMOHANA RAO done under our supervision, and has not been submitted elsewhere for a degree.

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# ABSTRACT

| | | |
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| Name of student | : | Paladugu Ramamohana Rao |
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The collisional deactivation rates of the $CO_2(00^\wedge 1)$ mode in binary mixtures with $CH_3OH$, $CH_3OD$, $C_2H_5OH$, $C_2H_4O$, $CH_3CHO$, $HCOOH$ and $CH_3COOH$ are experimentally measured in the temperature range of 300-750°K using the Laser Induced Fluorescence technique. The measured deactivation rates are in the range of $20-400(msec^{-1}torr^{-1})$ and decrease with increasing temperature suggesting that near-resonant V-V energy transfer processes are responsible for the deactivation. The processes are discussed for each binary system. In the alcohols, the C-O stretch mode dominates the deactivation process. In the other molecules, in addition to some fundamental bands around $1000 \ cm^{-1}$, some weak bands around $2350 \ cm^{-1}$ also participate. The dipole moments of the transitions involved in these processes are estimated using Sharma-Brau theory and our experimental results. This could not be done for the two acids, primarily because of substantial dimer concentration in the vapor phase at lower temperatures.

# CHAPTER I

## INTRODUCTION

The measurement and prediction of energy transfer rates in gases and gas mixtures is of practical importance in the design of new laser systems, chemical kinetics, gas dynamics, electrical discharges etc.

The importance of the knowledge of energy transfer rates in laser technology can be viewed from the tremendous impact that such a knowledge made on the $CO_2$ laser output power. From a level of 30 mW in pure $CO_2$, the power output has gone up to a few kilowatts in mixtures of $CO_2$-$N_2$-He[1-6]. This power enhancement and higher efficiency is closely related to the efficient energy transfer that occurs between the vibrational modes of $CO_2$ and $N_2$ and between the vibrational and translational modes of $CO_2$ and He. If the rate of excitation of the upper laser level becomes comparable to the decay rate of the lower laser level, over-population of the lower level limits the power output[7].

The performance limiting factors in molecular lasers are determined by the various energy transfer processes for the self deactivation and vibrational energy transfer of the constituent gases. At present not many molecules exhibit

laser action (even though the reported laser lines run into several hundreds) and it is reasonable to expect that more and more new molecular lasers will be developed as additional knowledge of energy transfer mechanisms and pathways in these molecules becomes available.

Atomic recombination and unimolecular chemical decomposition depend on the inter-and intramolecular energy transfer processes. Chemical reactions proceed through the rupture or weakening of chemical bonds. In conventional thermal reactions, energy is supplied to the translational degrees of freedom of the reactants which then has to be transfered into the internal degrees of freedom before the bond rupture or weakening takes place. However, vibrationally hot molecules undergo reaction even if their translational temperature is low. Thus, the rate at which energy is exchanged between the translational and vibrational (T-V) degrees of freedom and between vibrational and vibrational (V-V) degrees of freedom of the reacting molecules plays an important role in determining the rate of these reactions.

With the development of lasers, their application to induce and stimulate chemical reactions by vibrationally exciting the reactant molecules at even lower translational temperatures has attracted much attention[8-10]. When the

reactant molecule is excited using a laser, it is possible
that the energy gets redistributed among the translational
and the various internal modes of the molecule by collisions
before the chemical bond weakens. To understand the effect
of laser radiation on chemical reaction rates, product
yields etc. as well as the mechanism of unimolecular decom-
position, information regarding different energy transfer
processes like V-T and V-V is required.

However, in most systems it is difficult to measure
these rates directly. So it will be useful to have at least
some well tested theories, even if they are only approximate,
to predict these rates.

Before mentioning the energy transfer theories, it
is useful to classify the energy transfer processes. In
general they can be divided into several types like vib-
ration to vibration (V-V), vibration to translation (V-T),
vibration to rotation (V-R) and rotation to rotation (R-R)
processes. It is well established that R-R and V-R rates
are faster than V-V rates which are faster than V-T rates.
Of these, only the V-V energy transfer processes are stu-
died in this thesis. These can be further divided as[11]

1. Intermolecular V-V energy transfer

$$CO_2(00°1) + CO_2(0) \longrightarrow CO_2(0) + CO_2(11^10) + \triangle E = 272 \text{ cm}^{-1} \quad 1.1$$

$$CO_2(00°1) + N_2(v=0) \longrightarrow CO_2(0) + N_2(v=1) + \triangle E = 18 \text{ cm}^{-1} \quad 1.2$$

2. Intermolecular V-V energy sharing

$$CO_2(00°1) + CO_2(0) \longrightarrow CO_2(01^10) + CO_2(100) + \triangle E = 294 \text{ cm}^{-1} \quad 1.3$$

$$CO_2(00°1) + H_2O(0) \longrightarrow CO_2(01^10) + H_2O(010) + \triangle E = 87 \text{ cm}^{-1} \quad 1.4$$
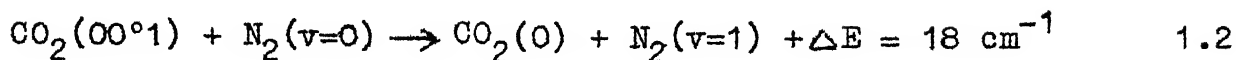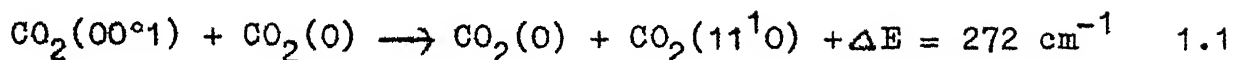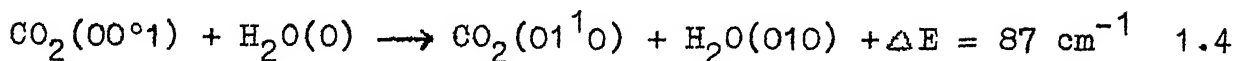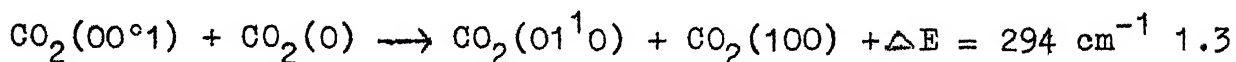
3. Intramolecular V-V energy sharing.

$$CO_2(00°1) + He \longrightarrow CO_2(04°0) + He + \triangle E = -199 \text{ cm}^{-1} \quad 1.5$$
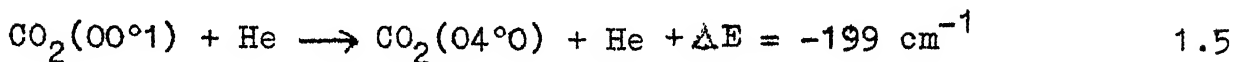
Each of the processes in the above classes may again be divided into
a) near-resonant processes i.e., those with small energy mismatch (processes 1.2 and 1.4) and
b) nonresonant processes ie., those with high energy mismatch (processes 1.1 and 1.3).

The observed V-V energy transfer probability in a polyatomic molecule may be due to one or more of the above class of processes[11]. For near-resonant V-V processes the energy transfer probabilities may be predicted using Sharma and Brau (SB) theory[12], whereas for nonresonant processes,

Schwartz, Slawsky and Hertzfeld (SSH) theory[13] and its refinements[14-17] may be used. SB theory takes into account only the long range multipole interactions and predicts comparatively large values for the energy transfer probability. It also predicts a negative temperature dependence for the energy transfer probability. However, it appears that this temperature dependence is not necessarily due to the long range nature of the intermolecular forces but arises, as pointed out by Moore[18], because of the "impact parameter, constant velocity, straight line form of the Born approximation" used in the theory. There is, infact, some recent controversy on this point[19-21]. On the other hand, the probabilities predicted by SSH theory, which assumes the presence of only short range repulsive forces, are generally considerably small even for near-resonant processes. In addition, this theory also predicts a positive temperature dependence for the probability. Hence, it may be said that whenever fairly large probabilities are encountered SB theory or some refinement of it[22,23] has to be used. Exceptions exist as in the case of Hydrogen halides, but in these systems it is now accepted that rotational effects are important[24]. SB theory has, infact, been extensively applied to many near resonant energy transfer processes involving small molecules like $CO_2$, $N_2$[14], $N_2$[15],

$C^{12}O, C^{13}O, N_2^{14}O, N_2^{15}O, N^{14}O, N^{15}O$ etc[18]. So it should be use-
ful to extend these studies to processes involving larger
molecules.

The collisional energy transfer rates in gases and
gas mixtures can be studied by creating large enough chan-
ges in the equilibrium populations among the vibrational
levels and the subsequent observation of the rate at which
the excess population relaxes to its equilibrium value. A
number of experimental methods are available to study these
rates[11,16]. Some of the widely used methods are

·1. Ultrasonic and shock tube techniques

2. Optical excitation without lasers

3. Flash photolysis

4. Monochromatically excited electronic fluorescence.

5. Chemical excitation

6. Molecular beams

7. Laser excitation methods

    (a) Laser induced fluorescence

    (b) Laser - Laser double resonance

    (c) Time resolved thermal lensing

All these methods have been thoroughly reviewed by
Moore[11], Amme[25] and Ormonde[26] and the references cited
therein. Among these, the laser excitation methods have been

widely used to obtain specific energy transfer rates[11,18,30] since lasers provide monochromatic and intense radiation which can be used to create large changes in energy level populations and to selectively excite any particular level among the internal degrees of freedom of a molecule. The possibility of exciting any given level in a molecule is becoming increasingly feasible with the availability of more and more tunable lasers.

In the present work, the rate of collisional transfer of energy from the $CO_2(00°1)$ mode in binary mixtures of $CO_2$ with several polyatomic molecules has been experimentally measured in the temperature range 300-750°K using the laser induced fluorescence technique. The polyatomic molecules studied are $CH_3OH$, $CH_3OD$, $C_2H_5OH$, $C_2H_4O$, $CH_3CHO$, $HCOOH$ and $CH_3COOH$. It has been observed that the deactivation rates are fairly large (20-400 $msec^{-1}torr^{-1}$) in all these systems and that they decrease with temperature. It is also shown in the following that several near-resonant processes are possible in each of these systems, and that the observed rate is due to a combination of all of them. Using the experimentally measured probabilities, the dipole moments of the transitions involved in these processes (except in the case of $HCOOH$ and $CH_3COOH$) are estimated assuming that SB theory is reasonably accurate in estimating the probabilities for

these processes. The estimated transition moments are necessarily approximate in view of the limitations of the SB theory pointed out above. However, these calculated moments are in accord with the relative spectral absorption intensities of the corresponding IR bands. Hence,if the values of these transition moments can be obtained through independent experiments, these estimates may be regarded as providing a basis to test the applicability of SB theory to near-resonant processes involving polyatomic molecules.

The remainder of the thesis is organised as follows. The laser induced fluorescence technique which is employed in the present work is described in detail in chapter II. The experimental setup along with a description of its components - namely  a) Q-switched $CO_2$ laser, b) signal detection units and c) signal processing units - have been briefly described in chapter III. In chapter IV, the collisional energy transfer rates obtained from the experiments in binary mixtures of the $CO_2$ ~~(0021) mode~~ with the polyatomic molecules listed earlier are discussed. The processes that are responsible for the energy transfer have been identified for each system and SB theory has been used to estimate the unknown transition dipole moments in these molecules. Finally, the conclusions are presented in chapter V.

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# CHAPTER II

## LASER INDUCED FLUORESCENCE TECHNIQUE

The laser induced fluorescence technique which has
been employed for V-V energy transfer studies in $CO_2$-poly-
atomic molecules is discussed briefly in this chapter. Ever
since this technique was reported[27,28] in 1966, it has been
widely used to study V-V and V-T/R energy transfer rates in
gases and gas mixtures in the temperature range of 77°K -
1000°K[11,18,29-33].

In general, any gas laser operating on a particular
vibrational transition permits that transition to be exci-
ted in that gas ( or a transition which can absorb that
frequency if a different gas is used) when a sample of it
is placed either inside or outside the laser cavity. A non-
equilibrium population results among the vibrational levels
of the absorbing gas following such an excitation. As the
population returns to equilibrium, primarily due to colli-
sional exchange of energy between the internal modes, fluo-
rescence emitted by any individual level can be followed by
an appropriate combination of filters and detectors to obtain
the rate of pumping to or the rate of removal of energy from
the fluorescing level. It is also possible to excite mole-
cules of one gas in a mixture of gases and follow the

fluorescence, if any, from the molecules of any of the other components of the gas mixture.

In the present work, a Q-switched $CO_2$ laser is used to excite the $CO_2$ molecules present in a test cell along with those of a polyatomic gas M. During the laser pulse the transitions (100, 020 $\longrightarrow$ 00°1) in $CO_2$ are saturated creating a non-equilibrium population among these levels. Immediately after the excitation pulse ceases, the excess population pumped into the (00°1) level, which leads to the emission of 4.3 $\mu$ fluorescence, starts decaying. The time constant $\tau$, of this decay, which is obtained by monitoring the 4.3 $\mu$ fluorescence, may be called the relaxation time or the life time of that level of the sample. In all our experimental runs single exponential decay of the fluorescence has been observed. This means that, if n(t) is the excess population in the (00°1) level at any time t after the excitation pulse is turned off, then the rate of change of this excess population is proportional to the excess population itself and is given by

$$\frac{dn}{dt} = -\frac{n}{\tau} \qquad\qquad 2.1$$

where $\tau$ is the relaxation time of the fluorescing level. The solution of this first order rate equation is

$$n = n_0 \exp(-t/\tau) \qquad\qquad 2.2$$

where $n_0$ is the excess population of the level at time $t = 0$.

The excess population of the (00°1) level returns to the equilibrium value through i) radiative decay, ii) collisions with $CO_2$ molecules and the molecules of the added gas, if any, and iii) diffusion to and subsequent decay by collisions with the walls of the container. Therefore, the total relaxation rate $(1/\tau)$ at a given pressure P can be written as

$$\frac{1}{\tau} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{coll}} + \frac{1}{\tau_{diff}} \qquad 2.3$$

The radiative decay rate $(1/\tau_{rad})$ is constant and is independent of gas pressure, while the collisional decay rate $(1/\tau_{coll})$ is directly proportional to the gas pressure P as long as only binary collisions are predominant. However, the diffusion rate $(1/\tau_{diff})$ varies inversely with the pressure and is important only if the sample pressure is low $(< 1 \text{ torr})$[34]. Therefore, the slope of the plot of $\tau^{-1}$ versus P yields $(P\tau_{coll})^{-1}$ directly, if we limit ourselves to $P < 1$ torr. This slope is called $K_{obs}$ in this thesis.

Since the $CO_2$(00°1) level is optically connected to the ground state, it emits spontaneous radiation at $4.3\,\mu$. The intensity of the emitted radiation is proportional to the excess number of molecules in that level. The rate at

which the excess population attains its equilibrium value
can be studied by monitoring the rate of decay of the flu-
orescence signal intensity with a Ge:Au detector maintained
at 77°K. If the decay is according to the exponential form
(equation 2.2), a semilogarithmic plot of the fluorescence
signal intensity versus time should yield a straight line
from which the relaxation time $\tau$ can be obtained. By measu-
ring $\tau$ at different pressures and then plotting $\tau^{-1}$ against
pressure P, one can obtain the collisional decay rate $K_{obs}$.
In a mixture of $CO_2$ and a polyatomic gas M, the collisional
rate thus obtained is due to: i) collisions with $CO_2$ mole-
cules and ii) collisions with molecules M. By studying the
composition dependence of $K_{obs}$, and then extrapolating $K_{obs}$
to zero percent composition of $CO_2$ in the mixture, it is
possible to deduce the collisional deactivation rate cons-
tant $K_{CO_2-M}$ of the $CO_2(00°1)$ mode with only M. The above
studies are carried out at different temperatures, to obtain
the tempreature dependence of the collisional deactivation
rates $K_{CO_2-M}$.

This laser excited fluorescence method has several
advantages over the conventional methods like flash photo-
lysis, ultrasonic absorption, shock waves etc., for the
measurement of energy transfer rates in gases and gas
mixtures[11]. The initial excited level of a molecule can be

precisely specified in laser experiments since the exciting
pulse emitted by the laser has very narrow band width. The
fact that this excitation can be achieved,without directly
disturbing the adjacent energy levels,has been used in
laser double resonance experiments. Thus,the excitation is
speific,and since decay from any other specific level can be
followed, deactivation rates can be measured experimentally
for specific levels. The other experimental methods are, in
comparison, limited by the fact that the excitation must
proceed through the translational degrees of freedom. Thus,
in these methods the excitation is not specific,and when
dealing with polyatomic molecules the analysis of the re-
sulting data is quite complex. Secondly, the high power
densities of the exciting radiation produced by lasers are
very useful in the study of fast V-V energy transfer rates
in gases and gas mixtures, since this enables one to satu-
rate the upper energy level of the absorbing transition,
which inturn yields a strong fluorescence signal with a
correspondingly high signal to noise ratio. The narrow band
width can be used to excite specific energy levels which is
not possible with other conventional methods.

The experimental data on energy transfer is generally
reported in terms of the deactivation rate constant $K_{CO_2-M}$,
the collision cross-section for energy transfer $\sigma$, and the

energy transfer probability per collision P. These are in-
terrelated as follows.

$$\bar{v} = K/nV \qquad\qquad 2.4$$

$$P = \bar{v}/\pi d^2 \qquad\qquad 2.5$$

where n = number density of molecules

V = average relative velocity of the colliding pair

and    d = average diameter of the colliding pair.

Thus for $CO_2$-M collisions

$$d = \tfrac{1}{2}\,[d(CO_2) + d(M)]$$

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# CHAPTER III

## EXPERIMENTAL SET UP

A brief description of the experimental set-up used to study Laser Induced Fluorescence had been reported[35,36]. A block diagram of the experimental set-up is shown in Fig.1. The main components of the set-up are

a) A Q-switched $CO_2$ laser

b) Fluorescence signal detection units

c) Signal processing units

A description of the above components is presented below.

a) Q-switched $CO_2$ Laser

The laser consists of a discharge tube; 25 mm ID, 3.5 m. long thick walled Pyrex glass. Glass 'T' joints are attached at both ends. The side projections are used as gas inlet and exit ports. One end of the discharge tube is sealed at Brewster's angle with a polished NaCl window (60 mm dia, 5 mm thick), and the other end is attached to a fixed mirror mount through flexible metal bellows. The gas inlet port is inturn connected to a copper tube which acts as a hollow cylindrical anode. The exit port is connected to a 160  1/m Welch mechanical pump through a water cooled copper tube, which acts as the cathode. The discharge tube is held
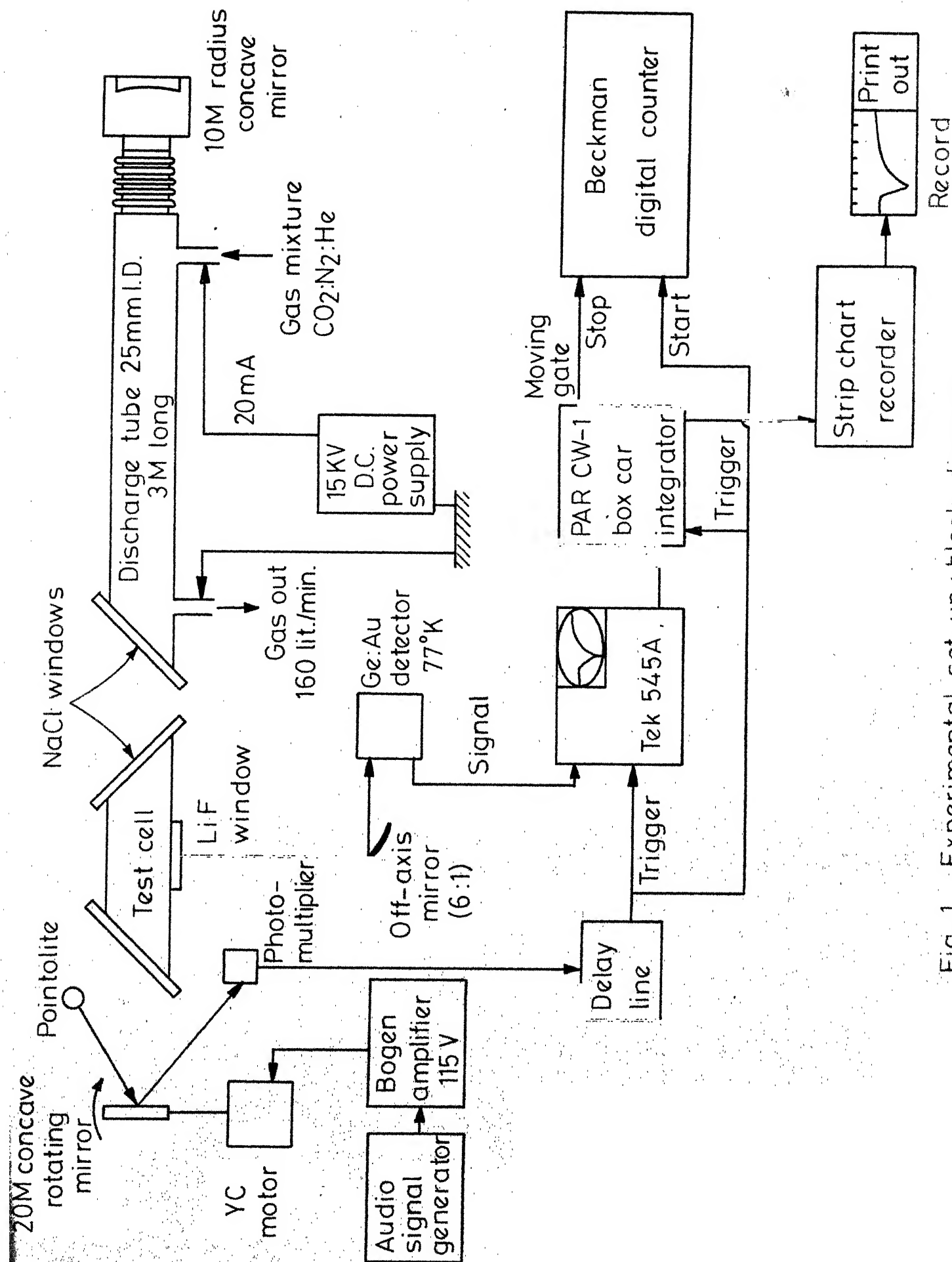
Fig. 1 — Experimental set-up : block diagram

concentric inside a 50 mm dia, 3 m long thick walled Pyrex glass tube. Cold water is circulated through the annulus to cool the plasma tube while in operation. The entire assembly is supported by 'V' blocks on a steel channel which is rigidly mounted on vibration proof concrete foundations.

Gold coated high reflectivity mirrors are used in the present work. The mirrors have been developed by vacuum deposition of gold on polished pyrex blanks. A 10 m. radius of curvature mirror with a 6 mm dia. central hole for laser power output coupling, is mounted in the stationary mirror mount. This hole is blanked by a NaCl window. The orientation of the mirror can be adjusted by two micrometer screws. The other mirror of 20 m. radius of curvature is mounted on the shaft of a Globe YC motor. This motor is located a meter away from the window fixed at Brewster's angle to facilitate the insertion of the fluorescence cell. Audio signal of 400 Hz is generated by an Exact Electronics function generator and amplified to 115 V through a Bogen amplifier. This power is used to run the YC motor at 40 Hz to Q-switch the laser. The motor is mounted on a steel plate which can traverse along both the horizontal and vertical axes. This plate is supported on a steel frame which can be tilted. These motions facilitate the easy alignment of the mirror.

The gases used in the laser are commercial grade Nitrogen supplied by Indian Oxygen Limited, Bone Dry grade $CO_2$ and high purity He both supplied by Matheson gas Co. The gases are mixed in the ratio of $CO_2:N_2:He = 1:2:1$ in a brass mixing chamber which is fitted with micrometer needle valves to regulate the flow of gases. The pressure in the mixing chamber is maintained at approximately 12 torr. The mixing chamber is connected to the discharge tube by a 10 m. long, 12 mm dia. teflon tube. The length of the teflon tube is selected such that the distance between the anode and the metal mixing chamber is at least twice that of the distance between the two electrodes to prevent the discharge occurring between the anode and the mixing chamber.

An optimum current of 18-20 mA through the discharge tube required a potential difference of 12 KV DC across the electrodes. The DC power supply for the laser consists of a high voltage transformer (15 KV-0-15 KV, 500 mA) and a series of rectifier diodes. The rectified voltage is filtered through a low pass filter net work and the output is taken to the plasma tube through a 100KΩ ballast resistor.

b) Fluorescence Signal detection units

The fluorescence cell which can be used upto 1000°K is described by I.V. Rao[37] and is shown in Fig.2. The cell

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NaCl window at Brewster angle

NaCl window at Brewster angle
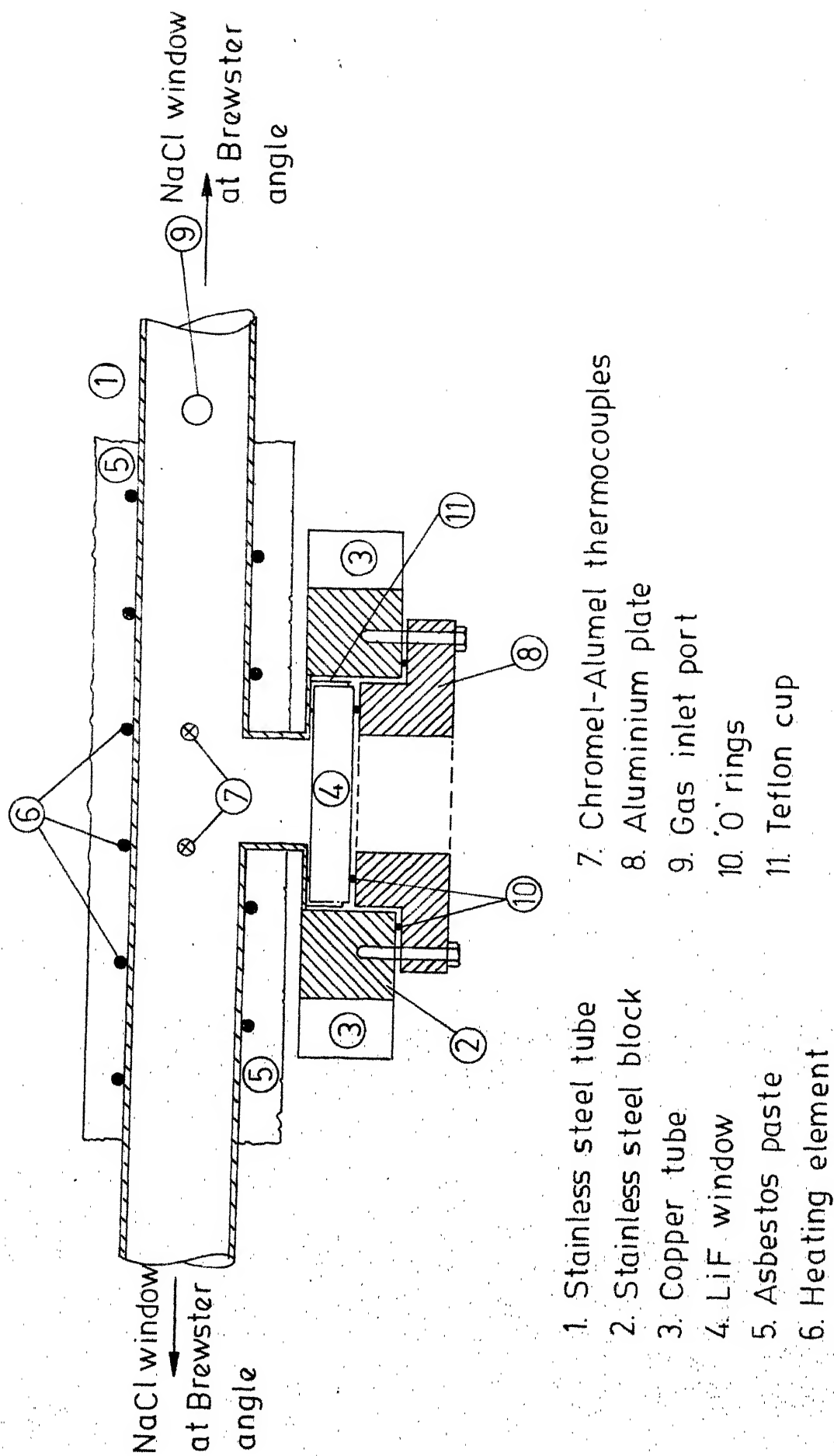
Fig. 2 - Sectional plan of the test cell.

1. Stainless steel tube
2. Stainless steel block
3. Copper tube
4. LiF window
5. Asbestos paste
6. Heating element

7. Chromel-Alumel thermocouples
8. Aluminium plate
9. Gas inlet port
10. 'O' rings
11. Teflon cup

is made of 35 cm long, 25 mm ID, 4 mm thick SS tube. To
either side of the SS tube, short glass tubes of the same ID
are attached by flanges. The ends of the glass tubes are
cut at Brewster's angle and sealed with NaCl windows. A 25-
mm hole is drilled at the center of the SS tube normal to
the axis on one side and a very short SS tube is then welded
after ensuring that its axis is perpendicular to the axis of
the main tube. A heavy SS block (10x10 cmx12mm) with a 25 mm
central hole is welded to the short side tube. This block,
which is kept cool by passing cold water through coils welded
to it, houses the LiF window which transmits 4.3 $\mu$ fluorescence
radiation and blocks not only the 10.6 $\mu$ laser radiation but
also any possible fluorescence from the polyatomic molecule.
On one side of the cell, a 6 mm hole is drilled at the top
which is connected through flexible metal bellows to a 6 mm
Pyrex ball joint, which can be coupled to the gas handling
station for evacuation and filling purposes. The cell is
wound with a 1000 W nichrome wire and insulated. Two Chromel-
Alumel thermocouples are located 2.5 cms. apart at the centre
of the cell to monitor the cell temperature. One of them is
used to measure and the other to control the temperature
through a Honey-Well on - off controller. The cell tempera-
ture is maintained constant within $\pm$ 2°C. The cell is placed
in the laser cavity between the discharge tube and the
Q-switch motor.

The test cell is evacuated down to $10^{-4}$ torr and the test gas mixture is filled at a known pressure. During the $CO_2$ Q-switched laser pulse, the transitions $(100,020) \longrightarrow 001$ in $CO_2$ gas present in the test cell are saturated. The $CO_2$ molecules excited to the $\nu_3$ state loose energy due to collisions with other molecules. The spontaneous emission from the transition $001 \longrightarrow 000$ in $CO_2$ at 4.3 μ is viewed through the LiF window. The fluorescence is collected by an off-axis elliptical mirror (6:1) and focussed on to a liquid Nitrogen cooled Ge:Au detector (SBRC) loaded with 10KΛ. The response time of the detector under these conditions is estimated to be less than 2 μsec.

c) Signal Processing Units

A point source of light is focussed on to the rotating mirror and its reflection is intercepted by an IP 28 photomultiplier biased at 900 V. The PMT output is used to trigger the Tektronix 545A Oscilloscope with predetermined delay. The detector output is displayed on the CRO with 1A7A plugin unit. The low and high frequency cut offs are adjusted to 1Hz and 1 MHz. The vertical amplifier output is fed to a PAR CW-1 Boxcar integrator to improve the signal to noise ratio. The delayed trigger output from the CRO is used to trigger the Boxcar and a Beckman digital counter.

Typical integration times are 20 m͞i͞n̄s̄ with a time constant of
0.1 ms, gate width of 1 $\mu$sec, to scan a time base of 100 $\mu$sec
with a 40 PPS pulse repetition rate. The moving gate of the
Boxcar is used to stop the counter. The output from the Box-
car is recorded on a Bausch-Lomb VOM-6 Strip Chart recorder.
A typical fluorescence decay curve as obtained on the recor-
der is presented in Fig.3.

## TEST SAMPLES

The polyatomic molecules chosen in this study are
liquids at room temperature with the exception of Ethylene
oxide. The test samples of these liquids are prepared as
follows. The liquid is taken into a 50 cc bottle which is
connected to the glass vacuum station. The trapped air is
first pumped out from this bottle. Then the sample is
frozen at liquid nitrogen temperature while evacuation is
continued for about 15 minutes. Then the sample is allowed
to warm up to room temperature and the vapors are pumped out
for another 15 minutes to get rid of any volatile impurities
that may be present. The vapors are then collected in tho-
roughly evacuated ($\simeq 10^{-4}$torr) glass bulbs at different
pressures. Then these bulbs are filled with $CO_2$ gas to bri-
ng the total pressure upto about 400 torr. The composition
of the sample in the bulbs is determined from partial
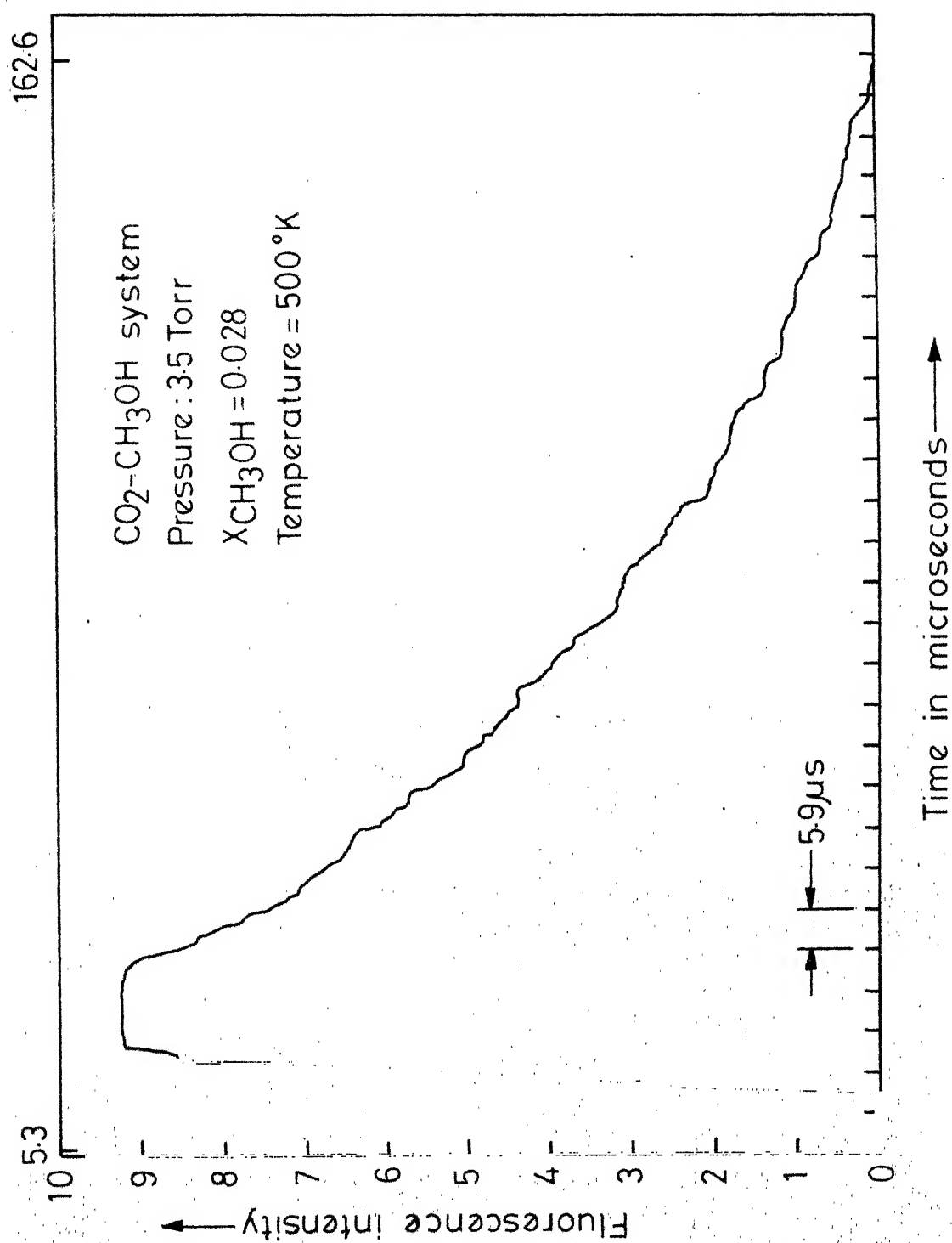
Fig. 3 – Typical fluorescence decay curve

pressure measurements. Pressures upto 25 torr are measured with a Silicone oil (Dow Corning 702 fluid) manometer, (accuracy 0.2 torr) while pressures higher than 25 torr are measured with a mercury manometer.

Same procedure is followed in the case of Ethylene oxide except that the bulbs are filled directly from the gas cylinder. In all the cases the mixtures are left for 24-36 hours to ensure complete mixing before a sample is withdrawn for fluorescence studies.

The purity of the samples used are as follows. $CO_2$ is 99.8% pure (Bone Dry grade, Matheson gas Co.) and $C_2H_4O$ is specified to be 99.7% pure (Union Carbide Co.).Among the liquids, the isotope $CH_3OD$ (supplied by Isotopes Division, BARC, Bombay) is stated to be grater than 95% isotopic purity. The purity of the samples HCOOH, $CH_3COOH$ and $CH_3CHO$ is stated to be 99%, 99.7% and 99.5% respectively (BDH,Analar grade).

The alcohols $CH_3OH$ and $C_2H_5OH$ are purified as follows. About 250 cc of laboratory grade alcohol is distilled over activated Calcium oxide. The distillate is mixed with about 2 grms. of Magnesium and a few crystals of Iodine and left over for 2-3 hours. Then the solution is distilled for two hours. The distillate,whose purity is greater than 99.5%, is used for subsequent sample preparation as described above.

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# CHAPTER IV

## RESULTS AND DISCUSSION

The deactivation of $CO_2(00^\circ1)$ mode in collisions with different polyatomic molecules has been studied using the Laser Induced Fluorescence technique as described in chapter II and III. The collision partners studied are $CH_3OH, CH_3OD,$ $C_2H_5OH$, $C_2H_4O$, $CH_3CHO$, $HCOOH$ and $CH_3COOH$. With each of these molecules as a collision partner, experiments have been carried out at different compositions of the mixtures and at different tempeatures. The measurements are limited to those compositions of the mixtures for which the measured relaxation times are about three to four times larger than the response time of the detector and the associated electronic circuitry, which is less than 2 $\mu$ secs. The observed decay rate $K_{obs}$ increases linearly with the composition $X_M$ of the colliding partner M in all the systems studied. The deactivation rate constant $K_{CO_2-M}$ is evaluated by linearly extrapolating $K_{obs}$ to zero percent of $CO_2$ since $K_{CO_2-M}$ referes to collisions between $CO_2$ and M only.

To check if dissociation is occuring in any of the samples in the temperature range studied, the following method has been used. The relaxation time $\tau$ of the sample at a pressure P is first measured at room temperature and

the temperature of the sample is then raised to the desired value and maintained there for an hour. Then the sample is cooled rapidly down to room temperature and the relaxation time and the pressure are measured again. If these agreed within the experimental error with the earlier ones, then it has been concluded that dissociation is unimportant. Each system is checked in this manner and the temperature range of the experiments is restricted such that no dissociation occurs.

In the temperature range of our measurements the de-activation rate constant is found to decrease with increasing temperature for all the systems studied. The magnitude of these rates and their decrease with temperature suggest that near-resonant vibration to vibration (V-V) energy transfer processes are primarily responsible for the transfer of energy from the asymmetric stretch mode of $CO_2$ to all the above mentioned molecules. As discussed in subsequent pages, the magnitude of the transition dipole moments of the transitions involved in $CH_3OH$, $CH_3OD$, $C_2H_5OH$, $C_2H_4O$ and $CH_3CHO$ in the deactivation of $CO_2(00^\circ1)$ mode have been estimated using the experimentally derived probabilities at different temperatures and SB theory.

The experimental results and their analysis are discussed for the individual systems in the following. The $CO_2$-$CH_3OH$ system is chosen as a prototype for a detailed discussion. Since the analysis of the data is similar for all the other systems, only a brief discussion is presented afterwards for the remaining systems.

$$CO_2 - CH_3OH$$
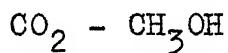
The energy transfer rates for the deactivation of $CO_2(00°1)$ mode have been measured for five compositions, all below 12.5%, of Methyl alcohol at three different temperatures, namely 305, 400 and 500°K. A typical fluorescence decay curve (P=3.5 torr, $X_{CH_3OH} = 0.028$ and T = 500°K) is shown in Fig.3. A semilogarithmic plot of this fluorescence signal intensity versus time, shown in Fig.4, resulted in a straight line, implying a single exponential decay which is also the case with all other signals. The slope of this line yields the relaxation time $\tau$ due to collisions. The relaxation times are measured at different total pressures for the same composition, in the range of 2-30 torr. Fig.5 shows the dependence of $\tau^{-1}$ on P, which is a straight line, suggesting that the deactivation is only through binary collisions in this pressure range. The slope of this line, which is the collisional decay rate $K_{obs} = (P \tau_{coll})^{-1}$, is found to be $2.75 \pm 0.09$ $msec^{-1}torr^{-1}$.

CO2-CH3OH system
Pressure=3.5Torr
$X_{CH_3OH}=0.028$
Temperature=500°K
$\tau^{-1}=20.9\ (msec)^{-1}$

5.9 μs

Intensity

Time in microseconds
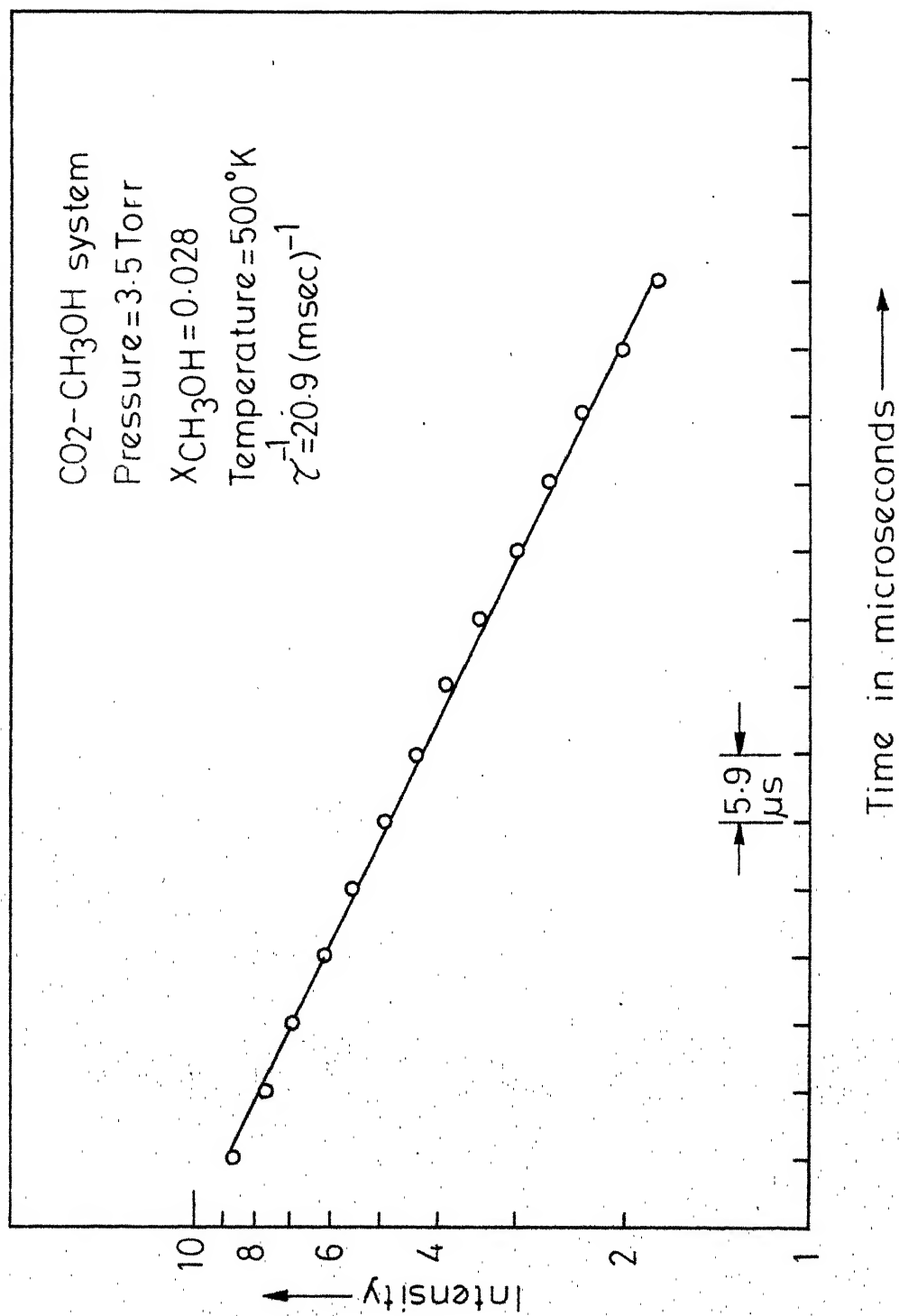
Fig. 4 — Semi logarithmic plot of fluorescence signal intensity vs. time.
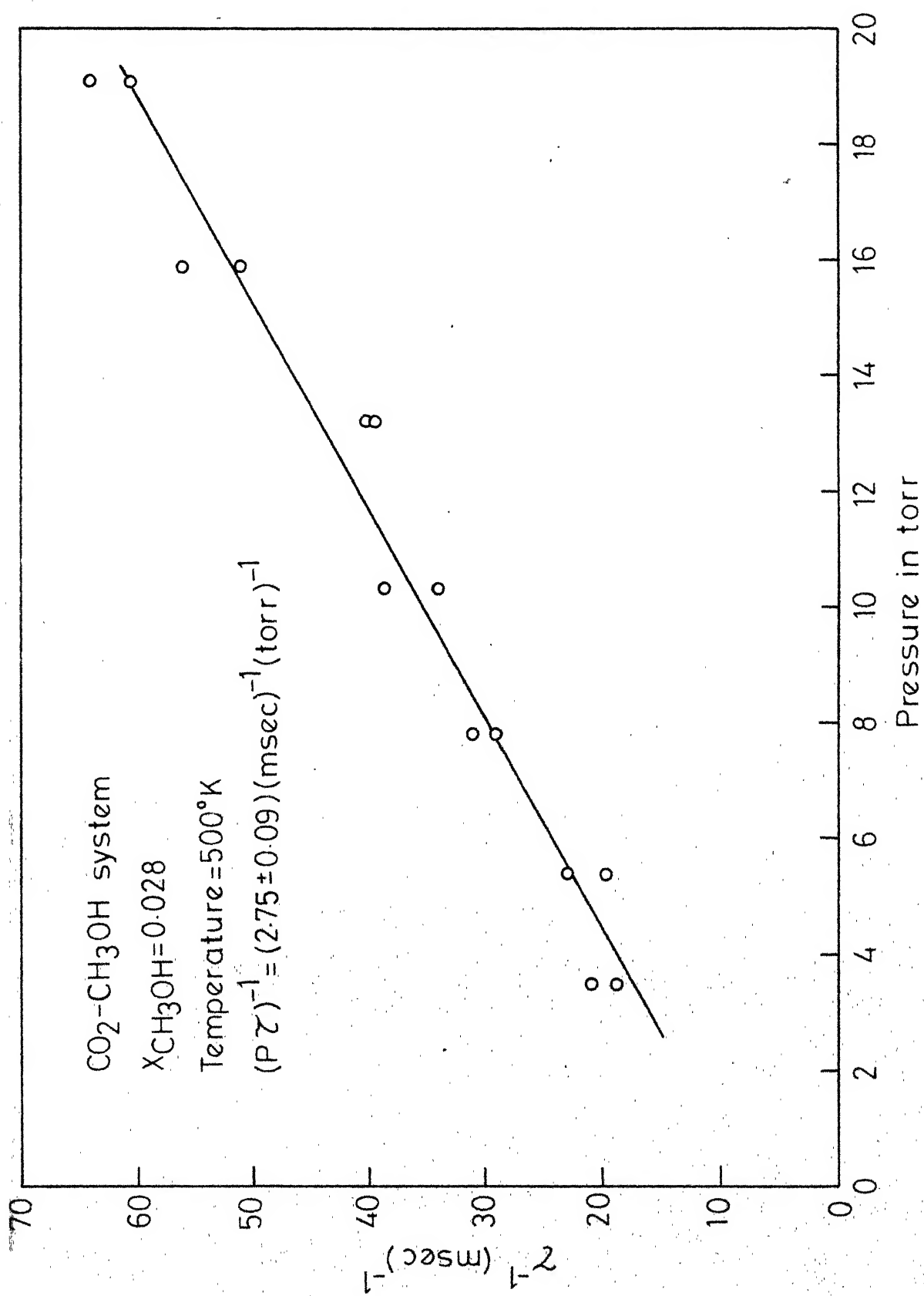
Fig. 5 - Plot of $\tau^{-1}$ with pressure.

$CO_2$-$CH_3OH$ system

$X_{CH_3OH} = 0.028$

Temperature = $500°K$

$(P\tau)^{-1} = (2.75 \pm 0.09)(msec)^{-1}(torr)^{-1}$

$\tau^{-1}(msec)^{-1}$

Pressure in torr

These measurements have been repeated for different compositions of the mixture and the observed decay rate increased with increasing mole fraction of the alcohol. This increase suggests that Methyl alcohol is more efficient in deactivating the $CO_2(00°1)$ mode than $CO_2$ itself. The composition dependence of the decay rate constant is shown in Fig.6. It can be seen from this plot that $K_{obs}$ varies linearly with the composition, $X_M$, of the colliding partner M in the mixture according to the relation

$$K_{obs} = K_{CO_2-CO_2} \, X_{CO_2} + K_{CO_2-M} \, X_M \qquad 4.1$$

Here, $K_{CO_2-CO_2}$ is the deactivation rate constant of the $CO_2(00°1)$ mode due to collisions with $CO_2$ molecules only[38], while $K_{CO_2-M}$ is the deactivation rate due to collisions with molecules M only and can therefore be obtained by extrapolating $K_{obs}$ to zero percent of $CO_2$ in the mixture.

This linear composition dependence of $K_{obs}$ has been found to hold in all the mixtures $CO_2$-M studied in this thesis. Therefore this extrapolation to zero percent $CO_2$ has been used in all the mixtures to obtain $K_{CO_2-M}$.

Experiments have been carried out at different temperatures and the results are shown in the form of a plot of $K_{CO_2-CH_3OH}$ versus temperature in Fig.7. It should be

CO₂-CH₃OH system

Temperature = 500°K

$K_{CO_2-CH_3OH} = 65.4 \pm 7.2 \, (msec)^{-1} (torr)^{-1}$

$K_{obs} \, (msec)^{-1} (torr)^{-1}$

Composition $X_{CH_3OH}$
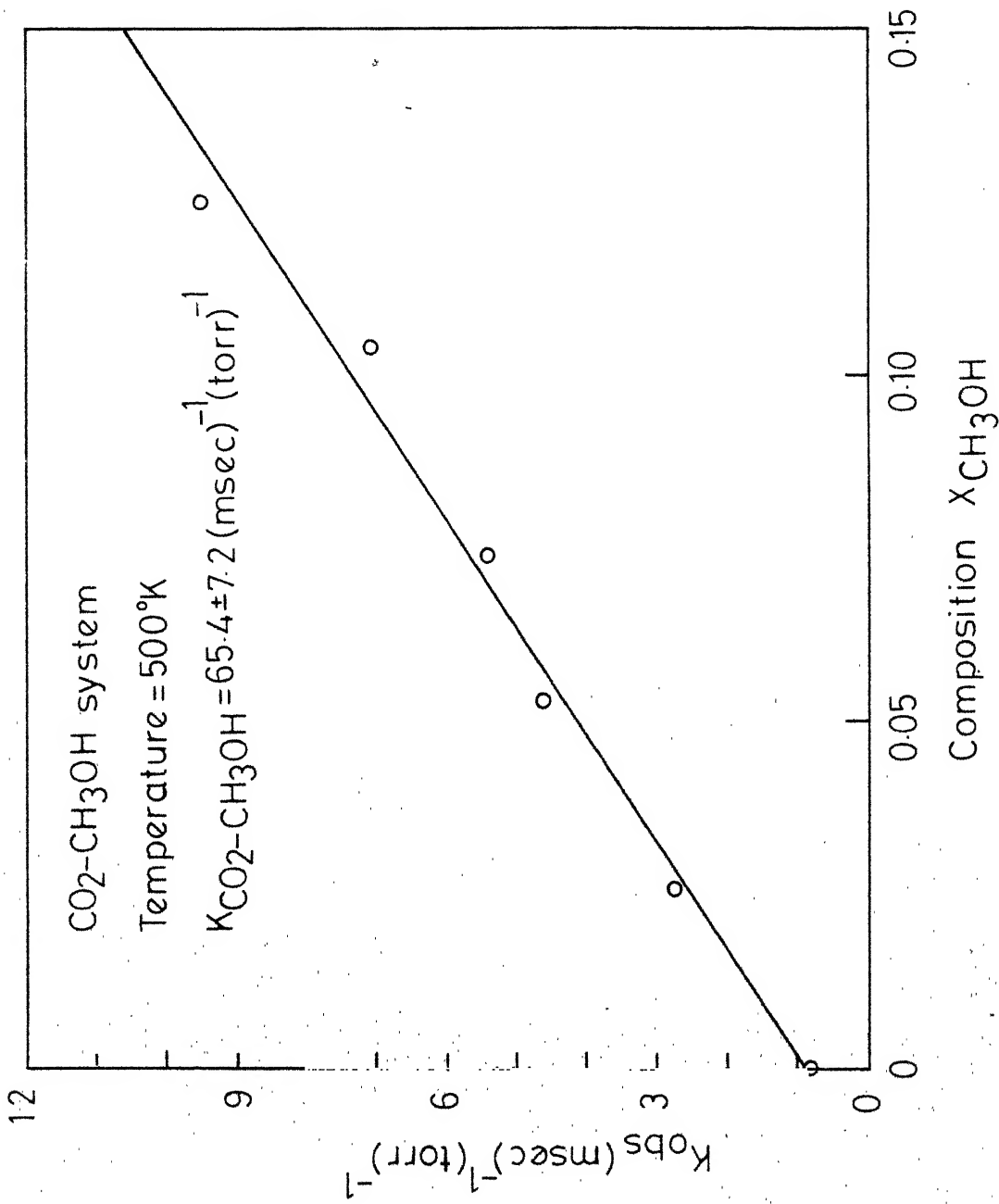
Fig. 6 — Composition dependence of the decay rate constant.
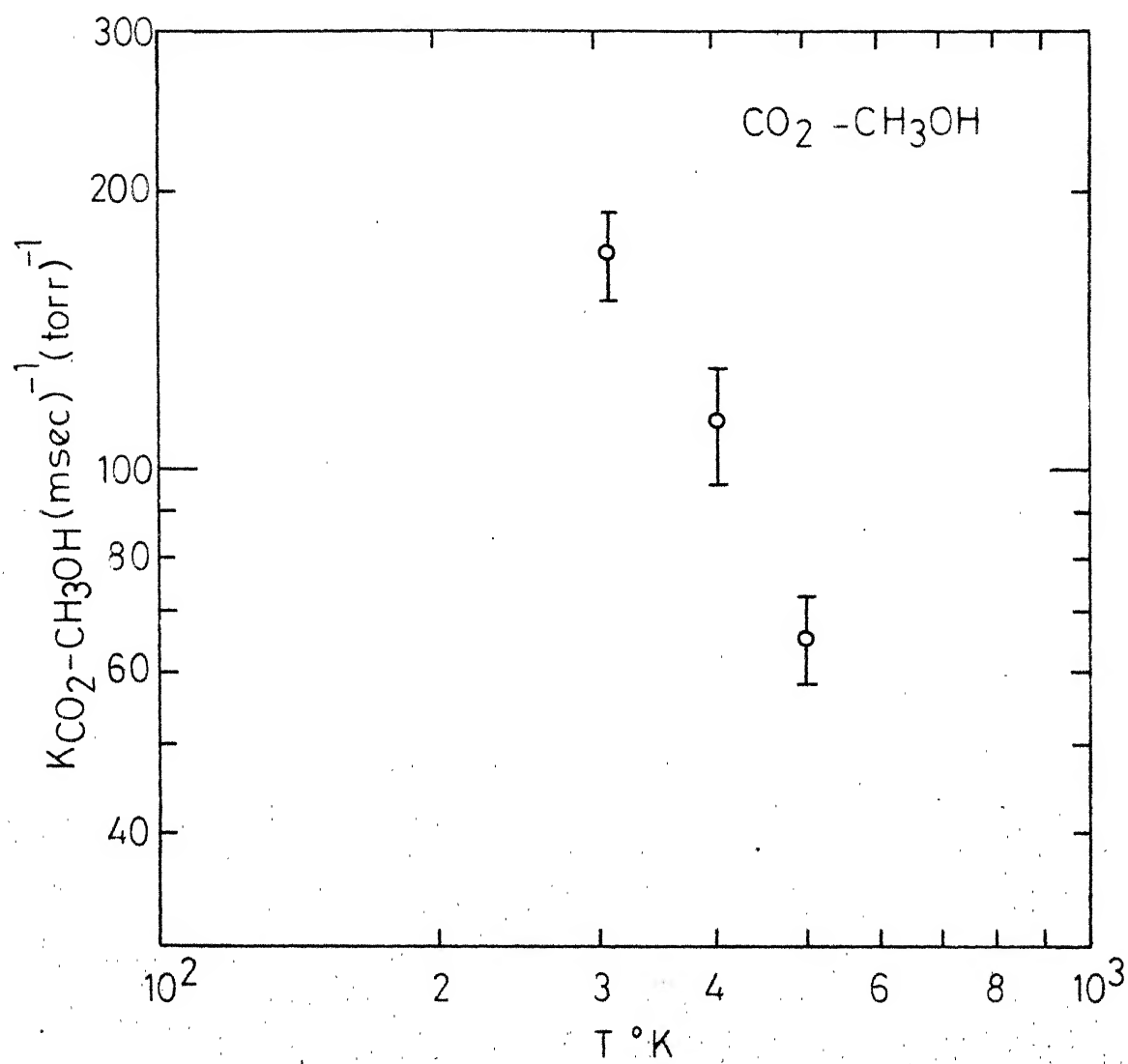
Fig. 7 – Temperature dependence of $K_{CO_2-CH_3OH}$.

pointed out that Agroskin et al.[**] measured the deactivation of $CO_2(00°1)$ mode with $CH_3OH$ at 300°K and found a value of 322 $msec^{-1}torr^{-1}$ whereas the present measurements resulted in a value of 172 $\pm$ 18 $msec^{-1}torr^{-1}$ at 305°K.

Energy transfer cross-section $\sigma$ and the experimentally derived probability $P_{exp}$ are calculated from the deactivation rate constant $K_{CO_2-CH_3OH}$ at different temperatures using equations 2.4 and 2.5 and are presented in Table 1. The complete experimental data for $CO_2-CH_3OH$ system is presented in Tables 2-4.

Table 1

Rate constants, cross-sections and probabilities of energy transfer from $CO_2(00°1)$ to $CH_3OH$*

| T°K | $K_{CO_2-M}(ms^{-1}torr^{-1})$ | $\sigma$ Å$^2$ | Px10$^2$ |
|---|---|---|---|
| 305 | 172 $\pm$ 18 | 0.92 $\pm$ 0.09 | 2.04 $\pm$ 0.22 |
| 400 | 112 $\pm$ 15.9 | 0.69 $\pm$ 0.09 | 1.53 $\pm$ 0.22 |
| 500 | 65.4 $\pm$ 7.2 | 0.45 $\pm$ 0.05 | 1.0 $\pm$ 0.11 |

* The error limits correspond to 95% confidence limits.

** This was quoted in Chemical Abstracts 81-70650 h, and the technique with which this was obtained was not mentioned. The original paper is in Russian language and is published in "Khim.Vys. Energ. 8,283 (1974)." This could not be refered to because of unavailability.

TABLE 2

TEMPERATURE (K)= 300.8     CARBONDIOXIDE-METHYLALCOHOL
(PRESSURE (P) IN TORR AND TAU INVERSE ($\tau^{-1}$) IN INVERSE MILLISEC(.))

| P | X = 0.228 $\tau^{-1}$ | P | X = 0.304 $\tau^{-1}$ | P | X = 0.374 $\tau^{-1}$ | P | X = 0.454 $\tau^{-1}$ | P | X = 0.552 $\tau^{-1}$ | P | X = 0.628 $\tau^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|

K(CBS)= 5.51± .53   K(CBS)= 7.25±0.08   K(CBS)= 5.40±0.26   K(CBS)= 4.58±0.34   K(CBS)= 2.75±.05

K(CO2-CH3OH)  65.4 ± 7.4(MILLISEC.TORR)$^{-1}$

## TABLE 3

CARBONDIOXIDE-METHYLALCOHOL-CL

TEMPERATURE (K)= 4?3.? 
PRESSURE (P) IN TORR AND TAU-INVERSE ($\tau^{-1}$) IN INVERSE MILLISEC )

| X = 0.104 | | X = 0.074 | | X = 0.043 | | X = 0.024 | |
|---|---|---|---|---|---|---|---|
| p | $\tau^{-1}$ | p | $\tau^{-1}$ | p | $\tau^{-1}$ | p | $\tau^{-1}$ |
| | | 20.2 | 164.2 | 15.3 | 99.2 | 24.2 | 54.9 |
| | | 20.2 | 154.0 | 15.9 | 101.2 | 24.7 | 51.3 |
| | | 16.2 | 138.5 | 13.1 | 72.7 | 22.7 | 74.0 |
| | | 16.2 | 141.9 | 10.6 | 63.2 | 22.8 | 71.9 |
| | | 13.0 | 112.1 | 10.6 | 65.6 | 20.? | 77.? |
| | | 16.0 | 107.0 | 8.6 | 51.? | 20.? | 70.6 |
| | | 16.? | 133.1 | 8.6 | 56.4 | 18.4 | 56.5 |
| | | 10.7 | 91.6 | 6.8 | 44.5 | 18.4 | 60.3 |
| | | 5.0 | 56.0 | 6.8 | 43.5 | 16.0 | 52.8 |
| | | 7.? | 76.0 | 5.6 | 42.1 | 16.0 | 57.1 |
| | | 5.0 | 64.6 | 6.6 | 40.4 | 12.? | 57.3 |
| | | 5.0 | 63.? | 4.3 | 33.? | 12.? | 55.9 |
| | | 6.6 | 65.? | 4.3 | 34.? | 12.? | 39.7 |
| | | 4.6 | 44.5 | 3.7 | 33.6 | 10.7 | 41.2 |
| | | 4.? | 42.5 | 3.7 | 31.8 | 7.1 | 35.0 |
| | | 3.7 | 41.4 | 3.0 | 22.? | 7.1 | 34.9 |
| | | 3.7 | 42.? | 3.0 | 26.0 | 4.? | 29.1 |
| | | 3.0 | 46.? | 2.6 | 26.2 | 4.7 | 29.6 |
| | | 3.0 | 40.7 | 2.6 | 25.? | 3.? | 22.0 |
| | | 2.4 | 33.2 | | | | 21.6 |
| | | 2.4 | 33.? | | | | |

K(PAS)= ?.?? K(CBS)= 7.34±0.01 K(CBS)= 7.34±0.04 K(CBS)= 5.32±0.04 K(CBS)= 2.74±0.02

K(CO2-CH3CH)=112±15.5 (MILLISEC.TORR)$^{-1}$

## TABLE 4

TEMPERATURE (K)= 30?.
CARBON DIOXIDE—METHYL ALCOHOL

PRESSURE (P) IN TORR AND TIME INVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.

| $X = 2.105$ | | $X = 0.074$ | | $X = 0.052$ | | $X = 0.026$ | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| | | 14.2 | 18?.? | 15.7 | 130.? | 14.4 | 83.3 |
| | | 14.2 | 171.0 | 15.7 | 130.? | 14.? | 83.6 |
| | | 12.5 | 172.5 | 13.8 | 118.8 | 13.? | 63.8 |
| | | 12.5 | 176.4 | 10.6 | 95.? | 13.? | 74.9 |
| | | 9.? | 140.? | 10.6 | 89.? | 12.1 | 69.6 |
| | | 9.? | 122.? | 9.8 | 101.0 | 12.1 | 63.2 |
| | | 8.6 | 85.1 | 9.8 | 95.4 | 1?.6 | 66.3 |
| | | 8.6 | 86.? | 7.2 | 73.? | 1?.5 | 60.7 |
| | | 5.? | 65.? | 7.2 | 69.? | 1?.4 | 60.7 |
| | | 6.? | 84.? | 6.2 | 72.? | 9.1 | 57.1 |
| | | 4.6 | 71.1 | 6.2 | 77.? | 6.? | 59.5 |
| | | 4.6 | 69.? | 4.? | 45.? | 6.? | 4?.3 |
| | | 3.? | 33.? | 4.9 | 58.? | 7.? | 44.2 |
| | | 3.? | 42.4 | 4.2 | 52.? | 5.9 | 39.5 |
| | | | | 4.2 | 47.? | 6.? | 39.2 |
| | | | | 3.4 | 3?.? | 5.0 | 41.5 |
| | | | | 3.4 | 36.9 | 4.1 | 28.9 |
| | | | | 2.9 | 39.? | 4.1 | 27.8 |
| | | | | 2.9 | 39.? | 3.4 | 26.8 |
| | | | | | | 3.4 | 32.1 |

K(OBS)= 12.58±0.14   K(OBS)= 12.58±0.14   K(OBS)= 7.47±0.01   K(OBS)= 4.28±0.04

K(CO2-CH2OH)=172±18         (MILLISEC.TORR)$^{-1}$

## General Comments

Any nonlinear polyatomic molecule contains, in addition to its 3n-6 (where n is the number of atoms in the molecule) fundamental vibrational bands, a large number of difference, combination and overtone bands. Hence a polyatomic molecule is likely to have several energy levels in any given energy interval and this number increases with the number of atoms in the molecule. Therefore many V-V energy transfer processes may occur during the collision of a $CO_2(00°1)$ molecule with any polyatomic molecule.

However, all these V-V processes may not contribute significantly to the deactivation of the $CO_2(00°1)$ mode. The magnitude of the observed deactivation rates and their decrease with temperature suggest that near-resonant V-V energy transfer processes are likely to play a major role in the deactivation of the $CO_2(00°1)$ mode. An idea of the relative contributions of these processes to the deactivation rate can be had by looking at the four points discussed below.

## 1. Energy mismatch ($\triangle E$)

In the following V-V process
$$CO_2(00°1) + CH_3OH(0) \longrightarrow CO_2(020) + CH_3OH(\nu_8 = 1033) + \triangle E = 30 \text{ cm}^{-1}$$

4.2
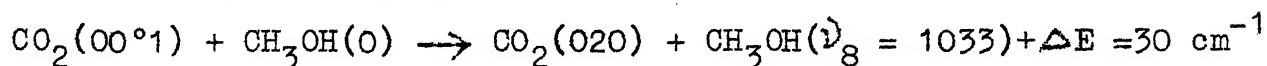
the energy that has been released by the $CO_2$ molecule has
not been completely taken up by the Methyl alcohol molecule.
This difference in the energy exchanged, which has to go
into the translational and rotational degrees of freedom of
Methyl alcohol, may be called the energy mismatch ($\triangle E$). If
$\triangle E$ in any process is small, typically less than about 100 to
150 cm$^{-1}$, that process is called a near-resonant process.
Theoretical calculations of Sharma and Brau, as well as the
more refined calculations that followed later, indicated that
the energy transfer probability falls off steeply in such
processes as the energy mismatch increases. Thus, $\triangle E$ is one
of the important indications of the relative magnitudes of
the transition probabilities for different V-V processes,
though exceptions to this exist as in the case of Hydrogen
Halides in which rotational effects are important[24].

## 2. Transition multipole moments

Sharma and Brau theory has indicated that the energy
transfer probability for a near resonant process is pro-
portional to the product of the multipole moments of the
transitions involved. Hence, processes involving weak bands,
i.e. difference bands, may be neglected in comparision with
processes involving strong bands, i.e. fundamentals, other
things being the same.

## 3. Quantum number changes

As Moore[39] has pointed out, it may be considered as a
rule of thumb that the probability for energy transfer to
occur during a collision decreases as the total number of
quantum number changes involved in the process increases.
Hence, other things being the same, processes that involve
less number of quantum number changes are more important.

## 4. Energy level populations

Molecules occupy different energy levels according
to the Maxwell-Boltzmann distribution. So, the number of
molecules in any energy level decreases exponentially as
the energy of that level increases. Thus, possibly except
at higher temperatures or when the first vibrationally
excited level is close to the ground state, transitions
originating from the ground vibrational state of the colli-
ding partner are predominant.

These criteria are used in the following to decide
whether a particular process can compete with other possi-
ble processes in contributing significantly to the total
deactivation probability.

# INTERPRETATION OF $CO_2$-$CH_3OH$ DATA

The fundamental vibrational frequencies of Methyl alcohol ($CH_3OH$) have been tabulated by Shimonouchi[40]. It was observed that this Alcohol is transparent to radiation with frequency around 2349 $cm^{-1}$[41] which corresponds to the $\nu_3 \rightarrow 0$ transition in $CO_2$. However, it has a very strong absorption band at 1033 $cm^{-1}$ ($\nu_8$) identified with the C-O stretch vibration and a weak absorption band at 1060 $cm^{-1}$ ($\nu_7$) identified with the $CH_3$ rock. Both these bands are near-resonant with the transitions $\nu_3 \rightarrow 2\nu_2$ and $\nu_3 \rightarrow \nu_1$ in $CO_2$. Thus, the transitions in $CH_3OH$ corresponding to these bands are likely to play a dominant role in the de-activation of $CO_2(00°1)$ through the following processes

$$CO_2(00°1)+CH_3OH(0) \longrightarrow CO_2(020)+CH_3OH(\nu_8=1033)+\Delta E = 30\ cm^{-1} \qquad 4.3$$

$$\longrightarrow CO_2(020)+CH_3OH(\nu_7=1060)+\Delta E = 3\ cm^{-1} \qquad 4.4$$

$$\longrightarrow CO_2(100)+CH_3OH(\nu_8=1033)+\Delta E = 73\ cm^{-1} \qquad 4.5$$

$$\longrightarrow CO_2(100)+CH_3OH(\nu_7=1060)+\Delta E = -100\ cm^{-1} \qquad 4.6$$
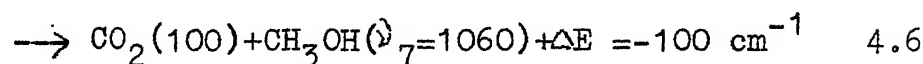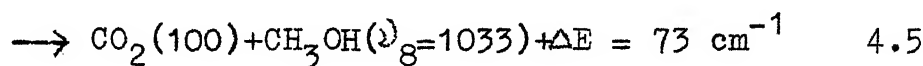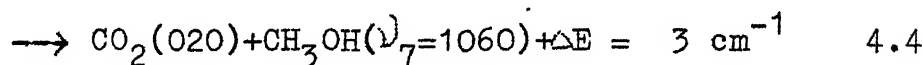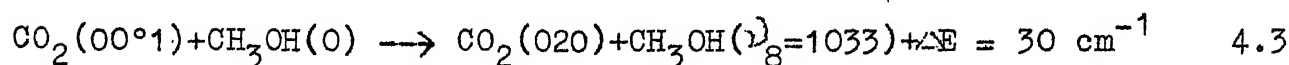
Process 4.6, in addition to involving a weak band ($\nu_7$) of the alcohol, involves a higher energy discrepancy ($\Delta E$) than the other processes. Thus, the contribution of this process to the total deactivation probability may be expected to be small and hence has been neglected in the following calculations.

## PROBABILITY CALCULATIONS

Landau and Teller[42] derived an expression for the temperature dependence of the energy transfer probability during a collision by a purely classical treatment for a vibration to translation (V-T) process. Assuming that only a repulsive exponential potential exists between the colliding molecules, they concluded that the probability varies as $\exp(-T^{-1/3})$. Later Schwartz, Slawsky and Herzfeld (SSH)[13] derived the same result with an approximate three dimensional quantum mechanical treatment. In the case of V-T processes, where the energy that has to be absorbed by or rejected into the translational degrees of freedom is large, the magnitudes and the temperature dependence of the energy transfer probabilities predicted using this theory are consistent with experimental results in many systems. In the limit of $\Delta E \longrightarrow 0$, i.e. for near-resonant processes, this theory predicted a positive temperature dependence. But the process

$$CO_2(00°1) + N_2(v=0) \longrightarrow CO_2(0) + N_2(v=1) + \Delta E = 18 \text{ cm}^{-1} \qquad 4.7$$
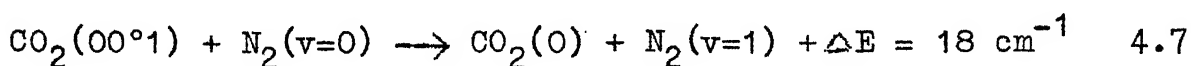
which is a near-resonant process, exhibited a negative temperature dependence in the range of 300-1000°K[38]. SSH theory not only failed to predict the observed negative temperature dependence but estimated a value for the probability at room temperature which is four times smaller than that observed.

Later, Sharma and Brau[12] developed a theory which takes into account long range intermolecular forces. This theory successfully predicted the magnitude and temperature dependence of the energy transfer probabilities for the process 4.7. Since then, this theory has been widely used to estimate the energy transfer probabilities for near-resonant processes[18,43-51]. Even though this theory predicts a negative temperature dependence for a near-resonant process, a positive temperature dependence is also predicted as $\triangle E$ is increased but the probabilities are considerably smaller. Recently, Sharma[52] showed that, refining the earlier theory by using Second order distorted wave Born approximation, does not improve the accuracy of the earlier simpler calculation while requiring a considerably larger computation time. Tam[22] has suggested a modification of the simpler theory. However, ~~it is felt that~~ in view of the other approximations in the method ( in fact, recently a controversy[19-21] has arisen about the origin of the $T^{-1}$ dependence obtained in this theory) the SB theory in its original form[12] has been employed in our calculations.

Further, in all the systems we will be considering in the following, none of the transition dipole moments required to calculate the probability by SB theory are available. So, in the following we have inverted the

procedure and estimated the transition moments using the experimentally measured probability. These estimated transition moments are approximate, and their reliability largely rests on the assumption that SB theory reasonably predicts the V-V transfer probabilities in these systems.

The experimentally derived probability can be written as

$$P_{exp} = \sum_i a_i \, p_i \qquad 4.8$$

where the summation extends over all the possible processes i that cause the energy transfer, $a_i$ is the square of the dipole moment of the transition of M involved in the process i and $p_i$ is the calculated energy exchange probability for the $i^{th}$ process using SB theory but assuming a value of unity for the square of the transition dipole moment of M. Then, a least squares method can be employed to obtain $a_i$. A similar method has been employed earlier to estimate the transition dipole moment of CS[51] and those of the $(\nu_3 + \nu_6) \longrightarrow 0$ and $(\nu_9 + \nu_{11}) \longrightarrow 0$ transitions in $C_2H_6$[37].

The molecular constants used in the calculations are given in Table 5. Methyl alcohol is assumed to be an oblate symmetric top molecule. The energy transfer probabilities calculated using the SB theory for the processes 4.3 to 4.5 are presented in Table 6.

Table 5

Molecular and other constants used in SB theory calculations

| Molecule | Hard sphere dia. $\sigma$ Å | Rotational constants $cm^{-1}$ | | | Ref. |
|----------|------|-------|-------|-------|------|
| | | A | B | C | |
| $CO_2$ | 4.0 | O | 0.39 | O | 53,69 |
| $CH_3OH$ | 3.585 | 0.793 | 0.822 | 4.26 | 53,54 |
| $CH_3OD$ | 3.585 | 0.733 | 0.781 | 3.65 | 54 |
| $C_2H_5OH$ | 4.455 | 1.11 | 0.304 | 0.267 | 53,56 |
| $C_2H_4O$ | 4.33 | 0.85 | 0.738 | 0.47 | 59 |
| $CH_3CHO$ | 3.585 | 1.888 | 0.339 | 0.304 | 68,69 |
| HCOOH | 4.455 | – | – | – | 70,68 |
| $CH_3COOH$ | 4.333* | – | – | – | 71 |

The squares of the transition dipole moments of $CO_2$ are[70]

$CO_2(\nu_3 \rightarrow 0) = 1.0 \times 10^{-37}$ $esu^2 cm^2$

$CO_2(\nu_3 \rightarrow \nu_1) = 1.44 \times 10^{-39}$ $esu^2 cm^2$

$CO_2(\nu_3 \rightarrow 2\nu_2) = 1.22 \times 10^{-39}$ $esu^2 cm^2$

*Calculated from critical constant, $V_c = 170.9$ $cm^3$/gm.mole

Table 6

Calculated Energy Transfer probabilities[*] for different
processes of $CO_2$-$CH_3OH$ system

| T °K | $p_3 \times 10^{-35}$ | $p_4 \times 10^{-35}$ | $p_5 \times 10^{-35}$ |
|------|------|------|------|
| 305 | 1.09 | 1.33 | 0.2414 |
| 400 | 0.86 | 1.01 | 0.2887 |
| 500 | 0.704 | 0.809 | 0.3095 |

It can be seen from the Table 6 that the sum of the probabilities for processes 4.3 and 4.5, both involving the $\nu_8 \longrightarrow 0$ transition in alcohol, is slightly larger than that for process 4.4. In addition to this, it may be infered from their relative IR absorption intensities[40] that the transition dipole moment for the process $\nu_7 \longrightarrow 0$ is considerably smaller than that of the $\nu_8 \longrightarrow 0$ transition. So, the process 4.4 can be neglected. The experimentally derived probability for this system can now be written as

$$P_{exp} = a\ (\nu_8 \longrightarrow 0)\ (p_3 + p_5) \qquad\qquad 4.9$$

where $p_3$, $p_5$ are the calculated probabilities using SB theory for the processes 4.3 and 4.5 while a ($\nu_8 \longrightarrow 0$) is the square of the dipole moment for the transition $\nu_8 \longrightarrow 0$.

[*] Values are obtained by assuming unity for the unknown transition dipole moments (squares) of M.

A least squares analysis of the data presented in Tables 1 & 6 yielded the following value for a $(\bar{\nu}_8 \longrightarrow 0)$

$$a(\bar{\nu}_8 \longrightarrow 0) = 1.33 \times 10^{-37} esu^2 cm^2$$

No attempt has been made to estimate the error limits to the transition dipole moments here and in the subsequent calculations, since the reported values are only approximate. However, more than the errors introduced by the least squares calculations, the limiting factor could be the applicability of SB theory for such calculations in polyatomic molecules. It is likely that short range repulsive forces may also contribute to the total probability when the energy discrepancy is larger $(\Delta E \gtrsim 100 \ cm^{-1})$. But the contribution due to these forces, which may be expected not to be large, has been ignored in this and the subsequent calculations. In the light of these comments the value of the squares of the transition dipole moments estimated in the present work, should be considered only approximate.

$$\underline{CO_2 - CH_3OD}$$
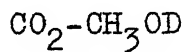
The deactivation of $CO_2(00°1)$ mode in collisions with Methyl alcohol-d ($CH_3OD$) has been studied for different compositions and at five different temperatures in the range of 300-600°K. As in the case of Methyl alcohol, the

fluorescence signal is observed to be a single exponential in all the experiments. The complete experimental data for the system $CO_2$-$CH_3OD$ is presented in Tables 7 - 11. The analysis of the data is similar to that of Methyl alcohol and hence the details are not repeated here. The temperature dependence of the deactivation rate constant $K_{CO_2-CH_3OD}$ is presented in Fig.8. The collision cross sections and the energy transfer probabilities calculated from this constant according to the equations 2.4 and 2.5 and are presented in Table 12 at different temperatures.

Table 12

Rate constants, cross-sections and probabilities of energy transfer from $CO_2(00°1)$ to $CH_3OD$

| T°K | $K_{CO_2-M}(ms^{-1}torr^{-1})$ | $\sigma~Å^2$ | $P_{exp} \times 10^2$ |
|---|---|---|---|
| 301 | 102.5 ± 8.2 | 0.55 ± 0.05 | 1.22 ± 0.07 |
| 375 | 93.9 ±14.7 | 0.57 ± 0.09 | 1.25 ± 0.19 |
| 450 | 71.6 ±11.6 | 0.47 ± 0.08 | 1.04 ± 0.17 |
| 525 | 46.4 ±10.9 | 0.33 ± 0.08 | 0.73 ± 0.17 |
| 600 | 57.0 ± 4.4 | 0.43 ± 0.03 | 0.96 ± 0.09 |

## TABLE 7

TEMPERATURE (K)= 600.0     CARBONDIOXIDE-METHYLALCOHOL-D

(PRESSURE (P) IN TORR AND TAU INVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.10 | | X = 0.075 | | X = 0.05 | | X = 0.025 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 10.3 | 75.1 | 14.5 | 99.1 | 13.9 | 63.1 | 23.0 | 63.0 |
| 10.3 | 76.2 | 13.5 | 85.4 | 13.9 | 66.1 | 21.0 | 64.9 |
| 10.3 | 81.2 | 13.5 | 83.0 | 12.1 | 63.1 | 18.9 | 58.0 |
| 9.8 | 80.9 | 12.1 | 70.5 | 12.1 | 50.5 | 18.9 | 57.8 |
| 9.7 | 63.9 | 12.1 | 74.9 | 10.2 | 50.4 | 16.6 | 48.4 |
| 9.0 | 72.2 | 10.4 | 72.2 | 10.2 | 57.8 | 16.6 | 54.5 |
| 9.0 | 63.0 | 10.4 | 57.9 | 8.2 | 58.7 | 14.4 | 53.7 |
| 9.2 | 69.2 | 9.7 | 51.1 | 8.2 | 45.1 | 14.4 | 45.2 |
| 8.7 | 69.7 | 9.7 | 56.2 | 6.5 | 31.5 | 12.6 | 44.7 |
| 8.6 | 63.0 | 7.6 | 48.9 | 6.5 | 54.1 | 12.6 | 43.6 |
| 8.0 | 65.7 | 7.6 | 51.1 | 4.8 | 28.6 | 8.3 | 37.3 |
| 6.0 | 56.0 | 6.5 | 42.0 | 4.8 | 28.0 | 8.3 | 32.6 |
| 6.2 | 54.4 | 6.5 | 38.0 | 3.4 | 23.1 | 6.4 | 23.0 |
| 5.7 | 69.2 | 5.0 | 34.7 | 3.4 | 25.7 | 6.4 | 22.9 |
| 5.7 | 47.6 | 5.0 | 51.6 | 2.6 | 28.6 | 4.2 | 20.4 |
| 4.6 | 37.6 | 3.6 | 28.1 | 2.2 | 23.3 | 4.2 | 21.7 |
| 4.6 | 37.2 | 3.6 | 26.9 | 2.2 | 19.1 | 3.0 | 17.1 |
| 3.8 | 30.0 | 2.6 | 22.2 | 2.6 | 21.8 | 3.0 | 16.7 |
| 3.4 | 28.6 | 2.6 | 22.3 | 2.2 | 18.6 | 2.4 | 17.7 |
| 2.2 | 23.0 | 1.9 | 30.3 | 2.2 | 17.5 | | |
| 2.2 | 24.6 | | | | | | |
| 1.7 | 24.9 | | | | | | |
| 1.7 | 21.4 | | | | | | |

K(OBS)= 6.74±0.02     K(OBS)= 5.30±0.05     K(OBS)= 3.99±0.10     K(OBS)= 2.64±0.01

K(CO2-CH3OD)= 66.9 ± 4.4 (MILLISEC.TORR)$^{-1}$

## TABLE 8

TEMPERATURE (K)= 525.0    CARBONDIOXIDE-METHYLALCOHOL-D

(PRESSURE (P) IN TORR AND $\tau^{-1}$ INVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.10 | | X = 0.075 | | X = 0.05 | | X = 0.025 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 12.6 | 92.6 | 15.8 | 81.7 | 16.2 | 69.8 | 19.3 | 54.3 |
| 12.1 | 89.2 | 13.7 | 71.9 | 14.2 | 51.5 | 17.9 | 53.2 |
| 12.3 | 90.9 | 13.7 | 66.7 | 12.8 | 48.3 | 17.9 | 46.0 |
| 11.8 | 83.0 | 11.6 | 58.6 | 12.6 | 52.3 | 16.3 | 52.7 |
| 11.8 | 87.6 | 11.8 | 52.8 | 12.9 | 58.3 | 15.4 | 47.2 |
| 7.4 | 65.6 | 10.6 | 66.8 | 11.3 | 46.8 | 15.4 | 39.9 |
| 7.4 | 53.0 | 10.6 | 57.7 | 11.3 | 51.7 | 14.5 | 41.6 |
| 6.4 | 54.2 | 10.6 | 40.7 | 9.7 | 42.4 | 14.5 | 39.4 |
| 6.4 | 56.6 | 6.7 | 41.6 | 9.7 | 43.8 | 14.5 | 39.2 |
| 6.4 | 55.7 | 6.7 | 49.4 | 8.2 | 33.5 | 11.1 | 28.9 |
| 5.6 | 47.0 | 6.7 | 38.3 | 8.2 | 38.7 | 11.1 | 31.7 |
| 5.7 | 41.? | 5.6 | 35.? | 6.1 | 29.4 | 9.6 | 28.1 |
| 4.7 | 39.? | 5.6 | 43.? | 6.1 | 28.3 | 9.6 | 28.7 |
| 4.1 | 45.5 | 4.2 | 24.9 | 4.6 | 25.7 | 7.8 | 24.3 |
| 3.1 | 39.2 | 4.2 | 38.1 | 4.6 | 21.6 | 7.2 | 26.8 |
| 3.1 | 34.3 | 4.2 | 24.2 | 3.0 | 23.2 | 6.2 | 21.7 |
| 1.6 | 19.6 | 3.0 | 25.6 | 3.0 | 17.7 | 6.2 | 21.8 |
| 1.6 | 17.4 | 3.0 | 32.7 | 1.6 | 12.9 | 3.4 | 13.6 |
| 1.0 | 11.9 | 3.0 | 32.5 | 1.6 | 14.3 | 3.4 | 15.3 |
| 0.7 | 12.3 | 1.7 | 21.8 | 2.2 | 17.5 | | |
| 0.7 | 24.6 | 1.7 | 19.9 | | | | |
| 1.7 | 24.8 | | | | | | |
| 1.7 | 21.5 | | | | | | |

K(OBS)= 6.14±0.11     K(OBS)= 3.65±0.10     K(OBS)= 3.49±0.02     K(OBS)= 2.49±0.03

K(CO2-CH3OD)= 46.3±16.5  (MILLISEC.TORR)$^{-1}$

TABLE 9

TEMPERATURE (K) = 450.0    CARBONDIOXIDE-METHYLALCOHOL-D
(PRESSURE (P) IN TORR AND TOW INVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.10 | | X = 0.075 | | X = 0.05 | | X = 0.025 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 15.8 | 129.9 | 16.9 | 94.7 | 15.4 | 84.2 | 21.2 | 58.6 |
| 15.8 | 139.1 | 14.2 | 95.4 | 15.4 | 70.2 | 21.2 | 60.3 |
| 15.8 | 122.0 | 11.0 | 64.7 | 15.4 | 68.4 | 18.4 | 57.9 |
| 15.9 | 149.8 | 11.0 | 57.0 | 12.6 | 64.5 | 18.4 | 58.3 |
| 12.2 | 110.0 | 11.0 | 70.1 | 10.1 | 45.5 | 15.2 | 46.8 |
| 12.2 | 115.7 | 9.0 | 62.8 | 9.8 | 51.9 | 12.1 | 41.0 |
| 12.2 | 116.6 | 9.0 | 60.5 | 8.0 | 45.6 | 12.1 | 42.3 |
| 9.8 | 97.8 | 7.0 | 48.5 | 8.0 | 45.7 | 8.7 | 28.9 |
| 9.8 | 91.7 | 7.0 | 52.0 | 6.4 | 38.1 | 8.7 | 32.9 |
| 7.8 | 75.7 | 7.0 | 52.6 | 6.4 | 35.6 | 7.8 | 33.7 |
| 7.8 | 63.6 | 5.8 | 49.2 | 5.2 | 31.5 | 7.8 | 25.7 |
| 6.4 | 57.9 | 5.8 | 46.4 | 5.2 | 32.0 | 5.6 | 22.3 |
| 6.4 | 57.0 | 4.6 | 33.5 | 4.1 | 28.1 | 5.5 | 22.1 |
| 5.0 | 39.4 | 4.6 | 37.5 | 4.0 | 30.5 | 5.0 | 21.1 |
| 5.0 | 42.1 | 3.8 | 33.1 | 3.4 | 23.0 | 5.0 | 26.7 |
| 4.2 | 46.4 | 2.9 | 24.8 | 3.4 | 21.0 | 3.7 | 17.1 |
| 4.2 | 45.5 | 2.9 | 27.5 | 2.6 | 24.1 | 3.7 | 19.0 |
| 3.2 | 36.6 | | | 2.6 | 21.8 | 2.4 | 16.2 |
| 3.2 | 35.7 | | | 2.2 | 18.6 | 2.4 | 17.7 |
| 2.7 | 32.5 | | | 2.2 | 17.5 | | |
| 2.7 | 33.8 | | | | | | |
| 1.7 | 24.8 | | | | | | |
| 1.7 | 21.5 | | | | | | |

K(OBS)= 9.18±0.24    K(OBS)= 4.98±0.04    K(OBS)= 4.15±0.05    K(OBS)= 2.44±0.03

K(CO2-CH3OD)= 71.6 ± 11.6(MILLISEC.TORR)$^{-1}$

## TABLE 10

CARBONDIOXIDE-METHYLALCOHOL-D

TEMPERATURE (K) = 375.0

(PRESSURE (P) IN TORR AND TOINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.10 | | X = 0.075 | | X = 0.05 | | X = 0.025 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 10.4 | 106.3 | 12.6 | 117.2 | 13.3 | 81.5 | 22.6 | 71.6 |
| 10.4 | 122.5 | 12.8 | 131.9 | 13.3 | 84.8 | 14.7 | 53.1 |
| 8.2 | 92.9 | 9.9 | 88.0 | 11.0 | 73.4 | 14.7 | 47.5 |
| 6.9 | 84.0 | 9.9 | 92.5 | 8.7 | 65.1 | 12.5 | 45.7 |
| 6.9 | 84.1 | 8.4 | 73.4 | 8.7 | 62.2 | 9.7 | 35.3 |
| 5.4 | 59.6 | 8.4 | 81.9 | 5.8 | 41.8 | 9.7 | 37.2 |
| 5.4 | 71.5 | 6.6 | 63.4 | 5.8 | 41.0 | 8.3 | 28.2 |
| 4.6 | 70.4 | 6.6 | 64.8 | 4.8 | 35.5 | 8.3 | 30.6 |
| 4.6 | 49.2 | 5.4 | 59.4 | 4.8 | 36.1 | 6.5 | 28.7 |
| 3.5 | 47.3 | 5.4 | 60.0 | 3.8 | 36.1 | 6.5 | 24.8 |
| 3.5 | 51.3 | 4.3 | 46.8 | 3.8 | 34.7 | 5.5 | 24.6 |
| 3.0 | 45.0 | 4.3 | 45.6 | 3.2 | 29.1 | 5.5 | 25.4 |
| 3.0 | 47.1 | 3.7 | 39.3 | 3.2 | 29.0 | 4.4 | 20.9 |
| 2.3 | 43.1 | 3.7 | 40.0 | 2.6 | 24.4 | 4.4 | 19.2 |
| 2.3 | 43.2 | 2.9 | 35.9 | 2.6 | 28.6 | 2.9 | 19.8 |
| 4.2 | 46.4 | 2.9 | 38.5 | 2.2 | 23.3 | 2.9 | 19.4 |
| 4.2 | 45.5 | 2.5 | 31.2 | 2.2 | 19.1 | 3.7 | 19.0 |
| 3.2 | 36.6 | 2.5 | 29.6 | 2.6 | 21.8 | 2.4 | 16.2 |
| 3.2 | 35.7 | 1.9 | 26.9 | 2.2 | 18.6 | 2.4 | 17.7 |
| 2.7 | 32.5 | 1.9 | 30.3 | 2.2 | 17.5 | | |
| 2.7 | 33.8 | | | | | | |
| 1.7 | 24.8 | | | | | | |
| 1.7 | 21.5 | | | | | | |

K(OBS) = 9.16±0.17     K(OBS) = 8.51±0.11     K(OBS) = 5.56±0.13     K(OBS) = 2.75±0.05

K(CO2-CH3OD) = 94. ± 14.7 (MILLISEC.TORR)$^{-1}$

# TABLE 11

CARBONDIOXIDE-METHYLALCCHCL-□

TEMPERATURE (K)=301.0

(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.05 | | X = 0.025 | |
|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 14.1 | 104.9 | 15.8 | 62.5 |
| 14.1 | 96.0 | 15.8 | 67.2 |
| 12.3 | 94.5 | 13.8 | 65.9 |
| 12.3 | 90.0 | 13.8 | 51.4 |
| 11.3 | 95.2 | 11.8 | 60.7 |
| 11.3 | 86.8 | 11.8 | 60.7 |
| 10.6 | 87.0 | 9.3 | 55.5 |
| 9.9 | 69.9 | 9.8 | 52.5 |
| 8.8 | 75.9 | 8.8 | 46.7 |
| 8.6 | 66.9 | 8.8 | 52.3 |
| 7.5 | 58.3 | 6.5 | 49.5 |
| 7.8 | 75.3 | 6.9 | 39.1 |
| 7.8 | 62.0 | 5.3 | 43.1 |
| 7.3 | 71.2 | 5.3 | 40.9 |
| 7.3 | 70.1 | 3.8 | 33.7 |
| 6.2 | 58.5 | 3.8 | 37.3 |
| 5.4 | 51.6 | 2.4 | 35.5 |
| 5.3 | 14.1 | 2.4 | 31.8 |
| 5.9 | 11.8 | 2.4 | 33.6 |
| 3.9 | 12.3 | 1.7 | 21.8 |
| 2.2 | 24.6 | 1.7 | 15.9 |
| 1.7 | 24.8 | | |
| | 21.5 | | |

K(OBS)= 5.42±0.13          K(OBS)= 2.57±0.06

K(CO2-CH3OC) = 102.5 ± 8.2(MILLISEC.TORR)$^{-1}$
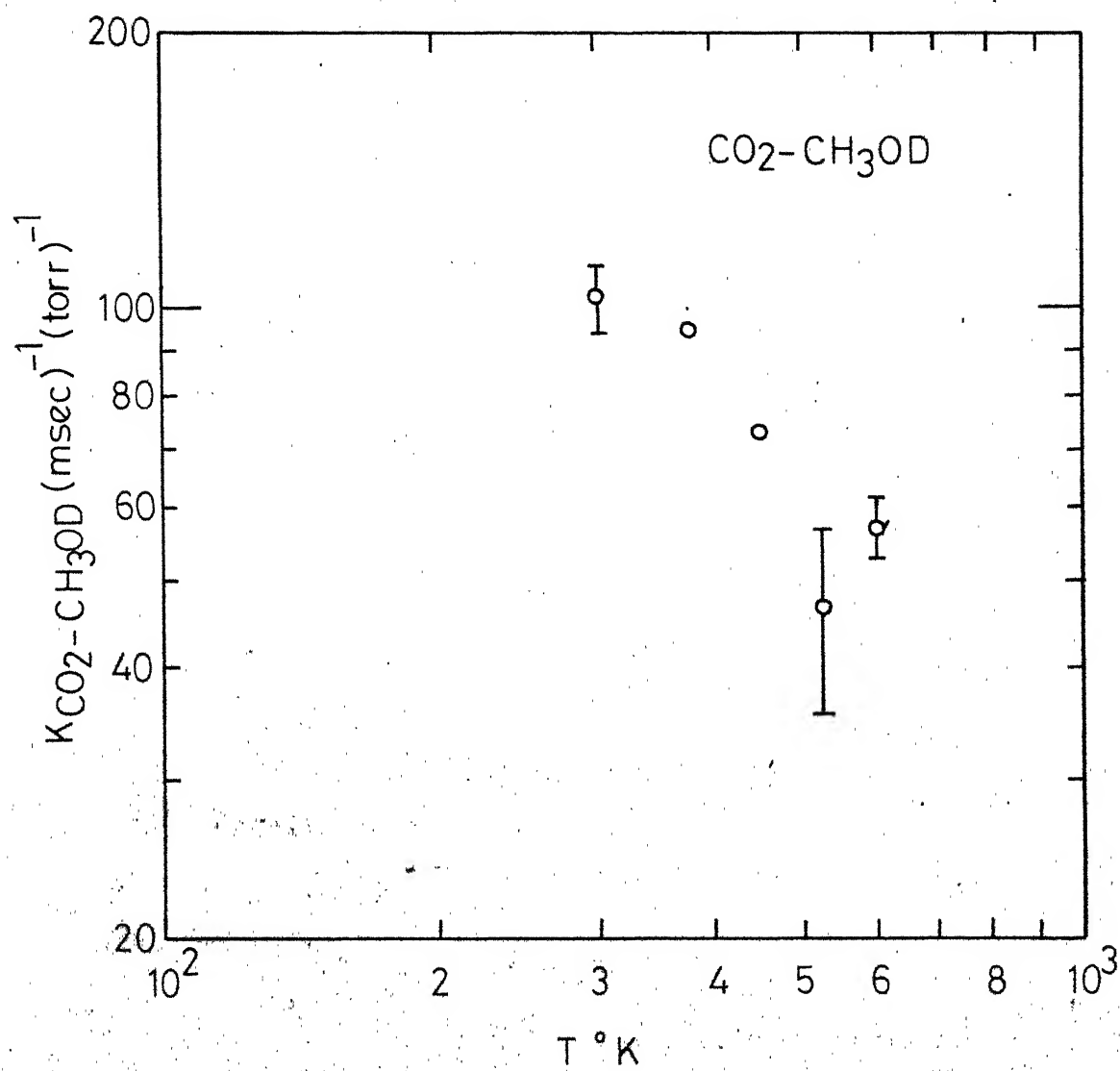
Fig. 8 – Temperature dependence of $K_{CO_2-CH_3OD}$.

## INTERPRETATION OF RESULTS

The decrease with temperature and the magnitude of the deactivation rates suggest that long range multipole interactions are primarily responsible for the transfer of energy from the asymmetric stretch mode of $CO_2$ to Methyl alcohol-d. The fundamental vibrational frequencies of this molecule are tabulated by Shimanouchi[40]. This alcohol is also transparent to radiation with frequency around 2349 cm$^{-1}$[41] and hence it is unlikely that the transition $\nu_3 \longrightarrow 0$ in $CO_2$ will occur during collisions. The possible deactivation of $CO_2(00°1)$ can be through the $\nu_3 \longrightarrow 2\nu_2$ and $\nu_3 \longrightarrow \nu_1$ transitions since there are three fundamental frequencies in $CH_3OD$ that lie in the energy range of these transitions. These are: (i) a very strong band at 1040 cm$^{-1}$ ($\nu_8$) identified as the C-O stretch, (ii) a strong band at 864 cm$^{-1}$ ($\nu_6$) which is the O-D bend and (iii) a very weak band at 1160 cm$^{-1}$ ($\nu_{11}$) named as $CH_3$ rock. These bands are likely to deactivate the $CO_2(00°1)$ mode through the following processes

$$CO_2(00°1) + CH_3OD(0) \longrightarrow CO_2(020) + CH_3OD(\nu_8 = 1040) + \Delta E = 23 \text{ cm}^{-1} \quad 4.10$$

$$\longrightarrow CO_2(100) + CH_3OD(\nu_8 = 1040) + \Delta E = -80 \text{ cm}^{-1} \quad 4.11$$

$$\longrightarrow CO_2(100) + CH_3OD(\nu_6 = 864) + \Delta E = 96 \text{ cm}^{-1} \quad 4.12$$

$$\longrightarrow CO_2(020) + CH_3OD(\nu_{11} = 1160) + \Delta E = -97 \text{ cm}^{-1} \quad 4.13$$
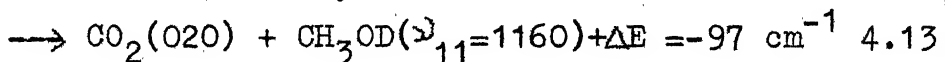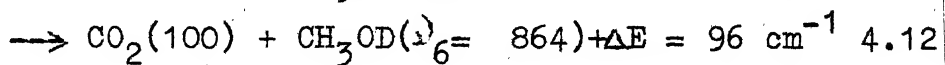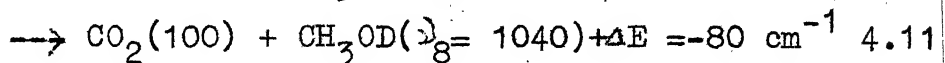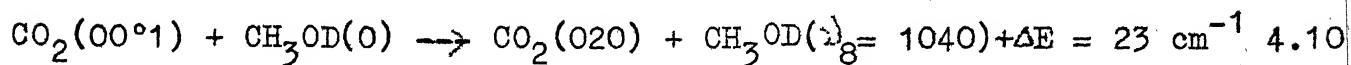
Even though the energy mismatches ($\triangle$E) in processes 4.12 and 4.13 are the same, the transition $\nu_{11} \longrightarrow 0$ is very weak and hence, the process 4.13 involving this transition can be neglected.

## PROBABILITY CALCULATIONS

The energy transfer probabilities for the processes shown in 4.10 - 4.12 have been calculated using SB theory taking into account dipole-dipole interactions. The molecular constants used in these calculations are listed in Table 5. The molecular diameter of $CH_3OD$ is assumed to be the same as that of $CH_3OH$. The transition dipole moments for the transitions involved for this alcohol are not available. The calculated probabilities for the above processes using SB theory, and assuming that this alcohol is an oblate symmetric top as in the case of Methyl alcohol, are presented in Table 13. They decreased with increasing temperature for process 4.10 for which $\triangle$E is small and increased as the temperature is increased for processes 4.11 and 4.12 where the energy mismatch ($\triangle$E) is somewhat larger.

The total deactivation probability for this system can be written as

$$P_{exp} = a(\nu_8 \longrightarrow 0)\ (p_{10} + p_{11}) + a(\nu_6 \longrightarrow 0)\ p_{12} \qquad 4.14$$

Table 13

Calculated Energy Transfer probabilities[*] for different

processes of $CO_2$-$CH_3OD$ system

| T°K | $p_{10} \times 10^{35}$ | $p_{11} \times 10^{35}$ | $p_{12} \times 10^{35}$ |
|-----|------|------|------|
| 301 | 1.207 | 0.1921 | 0.1081 |
| 375 | 0.9842 | 0.2368 | 0.1366 |
| 450 | 0.8322 | 0.2698 | 0.1641 |
| 525 | 0.7216 | 0.2909 | 0.1878 |
| 600 | 0.6373 | 0.3020 | 0.2064 |

where, as earlier, $P_i$ is the probability for the process
4.i and a's are the squares of the transition dipole moments.
A least squares analysis of the data presented in Tables 12 & 13
resulted in

$$a(\nu_8 \longrightarrow 0) = 0.9 \times 10^{-37} \text{ esu}^2 \text{cm}^2$$

$$a(\nu_6 \longrightarrow 0) = 0.16 \times 10^{-37} \text{esu}^2 \text{cm}^2$$

These moments are in agreement with the relative
intensities of the transitions as reported from spectro-
scopic measurements[40]. Thus the transition $\nu_8 \longrightarrow 0$, which
is termed very strong, is 6-7 times larger than that of
$\nu_6 \longrightarrow 0$ which is designated as strong.

[*]Values are obtained by assuming unity for the unknown
transition dipole moments(squares) of M.

## COMMENTS

The introduction of a Deuterium atom in the place of the Hydrogen atom has decreased the rate of the deactivation of the $CO_2(00°1)$ level by 100%. In Methyl alcohol the C-O stretch $\nu_8 \longrightarrow 0$ transition is deactivating the $CO_2$ asymmetric stretch level through both $\nu_3 \longrightarrow 2\nu_2$ and $\nu_3 \longrightarrow \nu_1$ transitions. In the Deuterated alcohol, in addition to the above mentioned processes, another strong transition $\nu_6 \longrightarrow 0$, the $CH_3$ rock, is also contributing to the deactivation. It should also be noted that our results indicate that Deuteration has reduced the strength of the C-O stretch band in Methyl alcohol (the transition dipole moment is reduced from 0.366 debye to 0.3 debye). However, both these bands are termed very strong. So the true moments of these bands should perhaps be a little closer.

### $CO_2-C_2H_5OH$
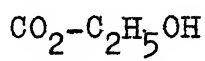
The quenching of the asymmetric stretching mode of $CO_2$ in collisions with Ethyl alcohol has been studied at different compositions at five temperatures in the range of 300-600°K. For all the runs taken, the semilogarithmic plot of fluorescence signal intensity versus time exhibited a straight line employing a single exponential decay. The complete experimental data at different temperatures for

this system is presented in Tables 14-18. The data has been analysed in a fashion similar to that of $CO_2$-$CH_3OH$ system and is not discussed here. The temperature dependence of the deactivation rate $K_{CO_2-C_2H_5OH}$ is presented in Fig.9. From these rates, the collision cross-sections and the energy transfer probabilities have been calculated and are presented in Table 19 at different temperatures.

### Table 19

Rate constants, cross-sections and probabilities of energy transfer from $CO_2(00°1)$ to $C_2H_5OH$

| $T°K$ | $K_{CO_2-M}(ms^{-1}torr^{-1})$ | $\sigma \overset{o}{A}^2$ | $P_{exp}×10^2$ |
|---|---|---|---|
| 301 | 209. $\pm$ 23.5 | 1.27 $\pm$ 0.18 | 2.27 $\pm$ 0.81 |
| 375 | 141 $\pm$ 5.8 | 0.96 $\pm$ 0.04 | 1.72 $\pm$ 0.07 |
| 450 | 101 $\pm$ 18.3 | 0.75 $\pm$ 0.19 | 1.35 $\pm$ 0.24 |
| 525 | 77.1 $\pm$ 6.6 | 0.62 $\pm$ 0.05 | 1.11 $\pm$ 0.1 |
| 600 | 70.2 $\pm$ 9.4 | 0.61 $\pm$ 0.08 | 1.08 $\pm$ 0.14 |

### INTERPRETATION OF RESULTS

A close observation of the deactivation rates presented in Table 19 reveals that the deactivation of the $CO_2(00°1)$ mode in collisions with Ethyl alcohol is again

## TABLE 14

### CARBONDIOXIDE-ETHYLALCOHOL

TEMPERATURE (K)= 600.0
(PRESSURE (P) IN TORR AND TOINVERSE $(\tau^{-1})$ IN INVERSE MILLISEC.)

| X = 0.075 | | X = 0.05 | | X = 0.025 | | X = 0.01 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 15.4 | 109.1 | 14.3 | 74.3 | 16.1 | 54.0 | 24.9 | 59.6 |
| 15.4 | 110.4 | 14.3 | 64.2 | 16.1 | 50.8 | 24.9 | 53.5 |
| 13.0 | 93.5 | 12.6 | 58.5 | 14.3 | 46.9 | 22.0 | 55.1 |
| 13.0 | 90.7 | 12.6 | 67.3 | 14.3 | 44.5 | 22.0 | 53.6 |
| 11.2 | 71.5 | 11.3 | 54.2 | 13.0 | 40.5 | 18.8 | 49.8 |
| 11.2 | 87.1 | 11.3 | 58.7 | 13.0 | 49.5 | 18.8 | 47.5 |
| 9.8 | 74.0 | 11.3 | 48.0 | 13.0 | 42.2 | 15.8 | 40.5 |
| 9.8 | 66.0 | 9.7 | 41.5 | 11.3 | 36.3 | 15.8 | 41.2 |
| 8.3 | 67.5 | 9.7 | 53.7 | 11.3 | 39.0 | 13.5 | 31.1 |
| 8.3 | 66.4 | 9.7 | 50.7 | 8.0 | 27.7 | 13.6 | 34.8 |
| 7.2 | 50.5 | 8.3 | 47.4 | 8.0 | 28.7 | 13.6 | 34.1 |
| 7.2 | 50.7 | 8.3 | 44.5 | 8.0 | 27.2 | 11.2 | 27.8 |
| 5.6 | 38.9 | 6.9 | 40.2 | 6.9 | 23.4 | 11.2 | 24.8 |
| 5.6 | 35.2 | 6.9 | 41.5 | 6.9 | 23.6 | 8.9 | 24.3 |
| 4.1 | 35.8 | 5.7 | 25.0 | 6.9 | 25.1 | 8.9 | 26.3 |
| 4.1 | 32.0 | 5.7 | 27.7 | 5.1 | 23.6 | 6.9 | 24.7 |
| 2.4 | 21.5 | 4.2 | 23.0 | 5.1 | 21.7 | 6.9 | 22.2 |
| 2.4 | 23.6 | 4.2 | 24.1 | 3.4 | 16.4 | 4.9 | 16.6 |
| 2.4 | 22.3 | 2.5 | 22.5 | 3.4 | 18.5 | 4.9 | 20.6 |
| 2.5 | 25.1 | 2.5 | 21.9 | 3.4 | 19.3 | 4.9 | 16.9 |
| 2.6 | 30.1 | 3.4 | 20.9 | 2.5 | 15.0 | 3.4 | 14.4 |
| 2.6 | 27.7 | | | 2.5 | 13.7 | 3.4 | 14.0 |
| | | | | 3.8 | 21.2 | 4.6 | 14.4 |
| | | | | 2.9 | 24.5 | 3.0 | 14.0 |
| | | | | | | 3.0 | 14.8 |

K(OBS)= 6.74±0.03    K(OBS)= 4.21±0.09    K(OBS)= 2.74±0.01    K(OBS)= 2.05±0.01

$K(CO_2-C_2H_5OH)= 70.2 \pm 9.4 (MILLISEC.TORR)^{-1}$

## TABLE 15

CARBONDIOXIDE-ETHYLALCOHOL

TEMPERATURE (K)= 525.0

(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.075 | | X = 0.05 | | X = 0.025 | | X = 0.01 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 15.7 | 140.1 | 15.7 | 82.8 | 19.2 | 75.9 | 27.0 | 50.1 |
| 15.7 | 108.1 | 15.7 | 73.0 | 19.2 | 62.2 | 27.0 | 51.0 |
| 13.1 | 96.6 | 14.2 | 62.0 | 17.3 | 59.3 | 23.9 | 41.0 |
| 13.1 | 90.2 | 14.2 | 78.9 | 17.3 | 56.6 | 23.9 | 39.8 |
| 13.1 | 83.7 | 12.6 | 75.9 | 15.6 | 61.0 | 20.8 | 37.5 |
| 12.0 | 84.1 | 12.6 | 74.2 | 15.6 | 47.4 | 20.9 | 39.5 |
| 12.0 | 93.1 | 11.2 | 53.0 | 14.3 | 42.2 | 18.7 | 41.3 |
| 12.0 | 92.9 | 11.2 | 55.7 | 14.3 | 47.9 | 18.7 | 39.3 |
| 10.1 | 75.4 | 9.9 | 51.4 | 12.3 | 45.8 | 16.6 | 32.7 |
| 10.1 | 81.9 | 9.9 | 47.1 | 12.3 | 38.1 | 16.5 | 35.4 |
| 8.2 | 69.7 | 8.6 | 50.6 | 10.8 | 39.6 | 13.8 | 32.8 |
| 8.2 | 62.0 | 7.2 | 41.5 | 10.8 | 38.2 | 13.8 | 28.7 |
| 7.2 | 54.0 | 7.2 | 41.4 | 9.2 | 38.4 | 10.5 | 27.4 |
| 7.2 | 56.8 | 5.8 | 37.8 | 9.2 | 37.8 | 10.5 | 26.7 |
| 5.4 | 42.2 | 5.8 | 34.8 | 7.5 | 27.7 | 8.2 | 22.5 |
| 5.4 | 46.8 | 4.1 | 30.2 | 7.5 | 31.8 | 8.2 | 24.2 |
| 3.5 | 39.6 | 4.1 | 28.7 | 7.5 | 33.6 | 6.2 | 25.4 |
| 3.5 | 31.9 | 2.4 | 21.8 | 5.8 | 25.2 | 5.8 | 16.0 |
| 3.5 | 35.9 | 2.4 | 21.9 | 5.8 | 27.6 | 5.8 | 18.1 |
| 2.6 | 25.1 | 2.4 | 21.1 | 5.8 | 24.0 | 5.8 | 16.9 |
| 2.6 | 30.1 | 3.4 | 20.9 | 3.8 | 20.4 | 3.7 | 15.9 |
| 2.6 | 27.7 | | | 3.8 | 21.1 | 3.7 | 15.7 |
| | | | | 3.8 | 21.2 | 4.6 | 14.4 |
| | | | | 2.9 | 24.5 | 3.0 | 14.0 |
| | | | | | | 3.0 | 14.8 |

K(OBS)= 6.70±0.01     K(OBS)= 4.31±0.01     K(OBS)= 2.85±0.02     K(OBS)= 1.40±0.01

K(CO2-C2H5OH)= 77.1 ± 6.6 (MILLISEC.TORR)$^{-1}$

# TABLE 16

TEMPERATURE (K)= 450.0    CARBON DIOXIDE-ETHYL...

(PRESSURE (P) IN TORR AND TOW INVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.075 p | $\tau^{-1}$ | X = 0.05 p | $\tau^{-1}$ | X = 0.025 p | $\tau^{-1}$ | X = 0.01 p | $\tau^{-1}$ |
|---|---|---|---|---|---|---|---|
| 11.0 | 109.2 | 13.8 | 103.6 | 16.3 | 51.9 | 21.3 | 31.3 |
| 11.8 | 111.3 | 13.8 | 102.3 | 16.3 | 63.0 | 21.3 | 34.4 |
| 11.8 | 107.9 | 12.0 | 80.6 | 15.3 | 51.9 | 18.8 | 33.8 |
| 10.6 | 102.0 | 12.0 | 84.0 | 15.3 | 50.3 | 16.3 | 34.9 |
| 10.6 | 104.9 | 11.0 | 76.5 | 13.8 | 54.6 | 15.9 | 35.0 |
| 9.3 | 91.7 | 9.2 | 59.8 | 13.9 | 49.0 | 15.9 | 29.9 |
| 9.3 | 86.4 | 9.2 | 54.5 | 12.8 | 54.5 | 15.9 | 34.7 |
| 8.0 | 76.5 | 7.2 | 60.3 | 12.2 | 47.0 | 14.2 | 29.2 |
| 8.0 | 77.2 | 7.2 | 50.4 | 12.2 | 51.8 | 14.2 | 28.2 |
| 7.2 | 72.1 | 6.2 | 47.2 | 12.2 | 44.5 | 12.3 | 22.6 |
| 7.2 | 75.9 | 6.2 | 49.1 | 9.8 | 41.1 | 12.3 | 22.4 |
| 6.2 | 59.9 | 5.5 | 39.5 | 9.8 | 34.7 | 10.8 | 20.5 |
| 6.2 | 67.3 | 5.5 | 40.3 | 8.1 | 34.7 | 10.8 | 22.3 |
| 5.3 | 60.6 | 4.6 | 42.2 | 8.1 | 31.6 | 9.6 | 20.9 |
| 5.3 | 55.9 | 4.6 | 39.2 | 6.4 | 27.3 | 9.6 | 22.0 |
| 4.3 | 52.1 | 3.8 | 30.4 | 6.4 | 29.3 | 9.6 | 21.7 |
| 4.3 | 51.8 | 3.8 | 31.4 | 6.4 | 31.9 | 7.8 | 17.6 |
| 2.4 | 39.4 | 2.4 | 23.0 | 5.2 | 27.0 | 7.8 | 17.7 |
| 2.4 | 45.4 | 2.4 | 18.9 | 5.2 | 26.9 | 5.5 | 20.3 |
| 1.8 | 30.7 | 2.4 | 21.1 | 4.2 | 22.3 | 5.8 | 20.3 |
|  |  | 3.4 | 20.9 | 4.2 | 23.0 | 3.6 | 14.9 |
|  |  |  |  | 3.0 | 21.0 | 3.6 | 13.6 |
|  |  |  |  | 3.0 | 20.4 | 4.6 | 14.4 |
|  |  |  |  | 2.9 | 24.5 | 3.0 | 14.0 |
|  |  |  |  |  |  | 3.0 | 14.8 |

K(OBS)= 7.50±0.25    K(OBS)= 6.59±0.01    K(OBS)= 2.81±0.01    K(OBS)= 1.21±0.02

K(CO2-C2H5OH)= 101±19.3    (MILLISEC.TORR)$^{-1}$

TABLE 17

TEMPERATURE (K)= 375.0                                    CARBONDIOXIDE-ETHYLALCOHOL
(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.075 | | X = 0.05 | | X = 0.025 | | X = 0.01 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 12.8 | 131.5 | 14.6 | 129.2 | 16.0 | 74.0 | 20.9 | 43.0 |
| 12.8 | 173.3 | 14.6 | 118.1 | 16.0 | 75.0 | 20.9 | 39.3 |
| 12.8 | 148.5 | 12.6 | 104.7 | 14.4 | 76.8 | 20.9 | 46.5 |
| 9.7 | 117.5 | 12.6 | 106.6 | 14.4 | 61.2 | 18.1 | 42.6 |
| 8.5 | 107.6 | 11.4 | 103.8 | 13.3 | 58.9 | 18.1 | 34.0 |
| 3.5 | 110.0 | 11.4 | 98.4 | 13.3 | 62.2 | 15.8 | 32.5 |
| 6.6 | 75.8 | 8.4 | 80.6 | 12.8 | 63.8 | 15.8 | 33.6 |
| 6.6 | 89.2 | 8.4 | 83.6 | 11.8 | 62.6 | 14.1 | 30.7 |
| 5.6 | 67.7 | 6.4 | 52.6 | 11.8 | 58.8 | 14.1 | 34.1 |
| 5.6 | 69.5 | 6.4 | 50.1 | 10.2 | 48.3 | 14.1 | 35.2 |
| 4.9 | 59.2 | 6.4 | 49.9 | 10.2 | 49.3 | 11.9 | 26.4 |
| 4.9 | 57.7 | 5.4 | 54.0 | 8.0 | 42.8 | 11.9 | 28.0 |
| 3.8 | 60.0 | 5.4 | 53.6 | 8.0 | 41.3 | 11.9 | 25.2 |
| 3.9 | 58.0 | 4.3 | 39.5 | 6.9 | 37.3 | 10.5 | 24.0 |
| 3.0 | 50.0 | 4.3 | 38.5 | 6.9 | 39.7 | 10.5 | 25.0 |
| 3.0 | 51.6 | 3.6 | 46.5 | 5.4 | 36.9 | 8.8 | 20.6 |
| 2.6 | 42.3 | 3.6 | 43.6 | 5.4 | 35.1 | 6.8 | 20.5 |
| 2.6 | 39.2 | 2.9 | 34.1 | 4.6 | 30.4 | 7.0 | 16.8 |
| 1.8 | 31.7 | 2.9 | 31.9 | 4.6 | 27.3 | 7.0 | 17.1 |
| 1.8 | 30.7 | 2.9 | 33.0 | 3.6 | 21.2 | 5.8 | 18.7 |
| | | 3.4 | 20.9 | 3.6 | 21.8 | 5.8 | 18.6 |
| | | | | 2.9 | 24.5 | 4.6 | 16.9 |
| | | | | 2.9 | 23.6 | 4.6 | 14.4 |
| | | | | 2.9 | 24.5 | 3.0 | 14.0 |
| | | | | | | 3.0 | 14.8 |

K(OBS)= 10.77±0.04        K(OBS)= 7.76±0.02        K(OBS)= 3.94±0.04        K(OBS)= 1.68±0.03

K(CO2-C2H5OH)= 141 ± 5.8   (MILLISEC.TORR)$^{-1}$

TABLE 18

TEMPERATURE (K)= 301.0     CARBONDIOXIDE-ETHYLALCO[

(PRESSURE (P) IN TORR AND TAU INVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.015 | | X = 0.01 | | X = 0.005 | |
|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 19.2 | 73.0 | 18.3 | 60.9 | 22.8 | 41.2 |
| 16.2 | 76.5 | 16.3 | 59.1 | 20.5 | 42.1 |
| 16.0 | 75.5 | 16.8 | 31.5 | 20.5 | 40.6 |
| 16.0 | 72.5 | 15.8 | 52.7 | 18.0 | 33.7 |
| 14.2 | 68.0 | 15.9 | 44.8 | 15.6 | 33.4 |
| 14.2 | 65.4 | 14.5 | 37.1 | 15.5 | 31.8 |
| 13.1 | 51.8 | 14.5 | 38.1 | 13.7 | 26.6 |
| 13.1 | 60.3 | 8.8 | 37.2 | 13.7 | 29.1 |
| 12.5 | 53.6 | 8.8 | 31.0 | 12.3 | 27.1 |
| 12.5 | 51.0 | 7.3 | 27.7 | 12.0 | 25.9 |
| 10.9 | 51.0 | 7.3 | 27.5 | 10.1 | 23.8 |
| 10.9 | 55.0 | 6.1 | 25.6 | 10.1 | 22.8 |
| 9.9 | 44.3 | 6.1 | 28.0 | 10.1 | 23.4 |
| 9.9 | 50.5 | 5.0 | 22.9 | 8.5 | 25.1 |
| 9.5 | 40.2 | 5.0 | 26.5 | 8.5 | 24.4 |
| 9.5 | 40.7 | 5.0 | 23.7 | 7.0 | 23.3 |
| 8.5 | 38.4 | 4.2 | 18.9 | 7.0 | 22.0 |
| 7.4 | 38.9 | 4.2 | 21.4 | 7.0 | 21.0 |
| 7.4 | | 3.4 | 19.5 | 5.6 | 19.6 |
| | | 3.4 | 21.5 | 5.6 | 18.9 |
| | | 3.4 | 20.9 | | |

K(OBS)= 3.56±0.02        K(OBS)= 2.09±0.01        K(OBS)= 1.32±0.01

K(CO2-C2H5OH)= 209±28.5   (MILLISEC. TORR)$^{-4}$
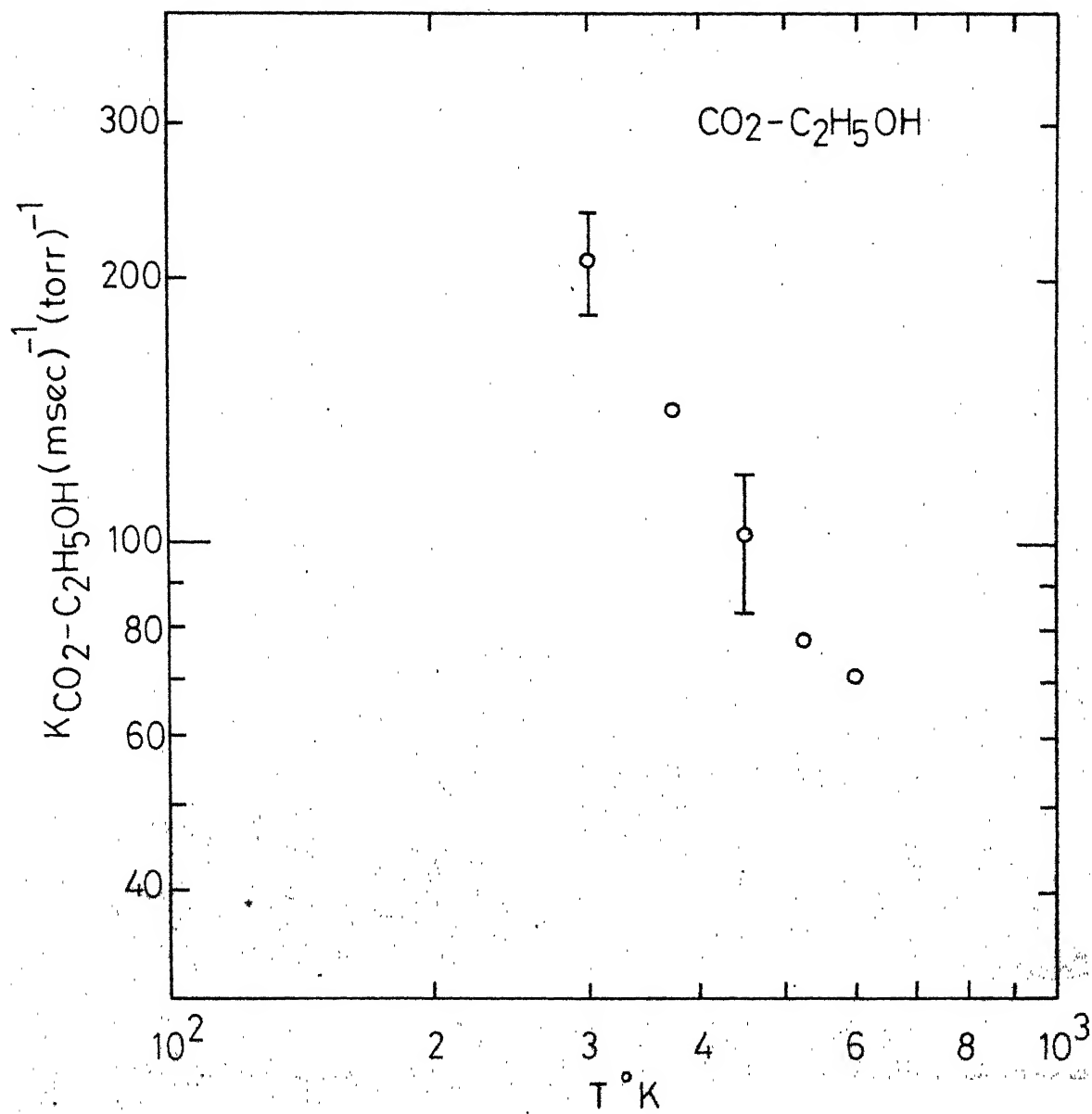
Fig. 9 – Temperature dependence of $K_{CO_2-C_2H_5OH}$

## PROBABILITY CALCULATIONS

The energy transfer probabilities have been calculated at different temperatures using SB theory for process 4.15 by taking into account only the dipole-dipole interactions and assuming a unit value for the two unknown $C_2H_5OH$ transition moments. Then the experimental probability can be written as

$$P_{exp} = a(\nu_x \rightarrow 0) \, p_{15} + a(\nu_4 \rightarrow 0) \, p_{16} \qquad 4.18$$

where a's are squares of the appropriate transition dipole moments. However, both the processes 4.15 and 4.16 have the same energy mismatch ($\Delta E = -4 \text{ cm}^{-1}$) and hence the same temperature dependence. Therefore, their ratio is given by the ratio of the squares of the transition moments of $CO_2$ as follows.

$$p_{15}/p_{16} = a(\nu_3 \rightarrow 0)/a(\nu_3 \rightarrow 2\nu_2) = 1 \times 10^{-37}/1.22 \times 10^{-39} \simeq 82 \qquad 4.19$$

Therefore

$$P_{exp} = [82 \, a(\nu_x \rightarrow 0) + a(\nu_4 \rightarrow 0)] \, p_{16} \qquad 4.20$$

The molecular constants used in the calculation of $p_{16}$ are given in Table 5. Ethyl alcohol is assumed to be a prolate symmetric top molecule. The results of the calculations for $p_{16}$ are presented in Table 20. A least square analysis of

this data according to equation 4.20 resulted in a value of $1.95 \times 10^{-37} esu^2 cm^2$ for the combined coefficient. Since $\nu_x \rightarrow 0$ is weak and $\nu_4 \rightarrow 0$ is very strong in $C_2H_5OH$, the ratio $a(\nu_4 \rightarrow 0)/a(\nu_x \rightarrow 0)$ is likely to be between 1000 to 100. For these limiting ratios the square of the dipole moment of the C-O stretch can be estimated from equation 4.20 as $1.8 \times 10^{-37}$ and $1.07 \times 10^{-37} esu^2 cm^2$ respectively.

Table 20

Calculated Energy Transfer probabilities[*] for process 4.16

of $CO_2-C_2H_5OH$ system

| T°K | $p_{16} \times 10^{-35}$ |
| --- | --- |
| 301 | 1.091 |
| 375 | 0.8783 |
| 450 | 0.7354 |
| 525 | 0.6339 |
| 600 | 0.5579 |

COMMENTS

This study reveals that all the three alcohols are very efficient in deactivating the $CO_2(00°1)$ mode. In all the three cases studied, it has been observed that the very

[*] Values are obtained by assuming unity for the unknown transition dipole moments (squares) of M.

strong C-O stretch vibrational transition is mainly respon-
sible for the deactivation. The unknown transition dipole
moments for the C-O stretch mode in all the three alcohols
studied are estimated though only very approximately for
$C_2H_5OH$. The deactivation rate is about the same for the
two alcohols $CH_3OH$ and $C_2H_5OH$.

$$CO_2-C_2H_4O$$
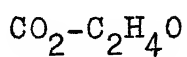
The collisional deactivation of $CO_2(00^\circ1)$ mode with
Ethylene oxide which has the same molecular weight as that
of $CO_2$, has been studied at four different compositions in
the temperature range of 300-650°K. The fluorescence signal
intensity again displayed a single exponential decay for all
the experimental runs taken. The deactivation rates
$K_{CO_2-C_2H_4O}$ are estimated at different temperatures by ana-
lysing the data in the same lines as in the case of $CO_2-CH_3OH$
system, and the temperature dependence of the rate is plotted
in Fig.10. The complete experimental data has been presented
in Tables 21-28 at different temperatures. The experimental
cross-sections and the energy transfer probabilities cal-
culated from the deactivation rates by using equations
2.4 and 2.5 are presented in Table 29 along with the rate
constants at different temperatures.
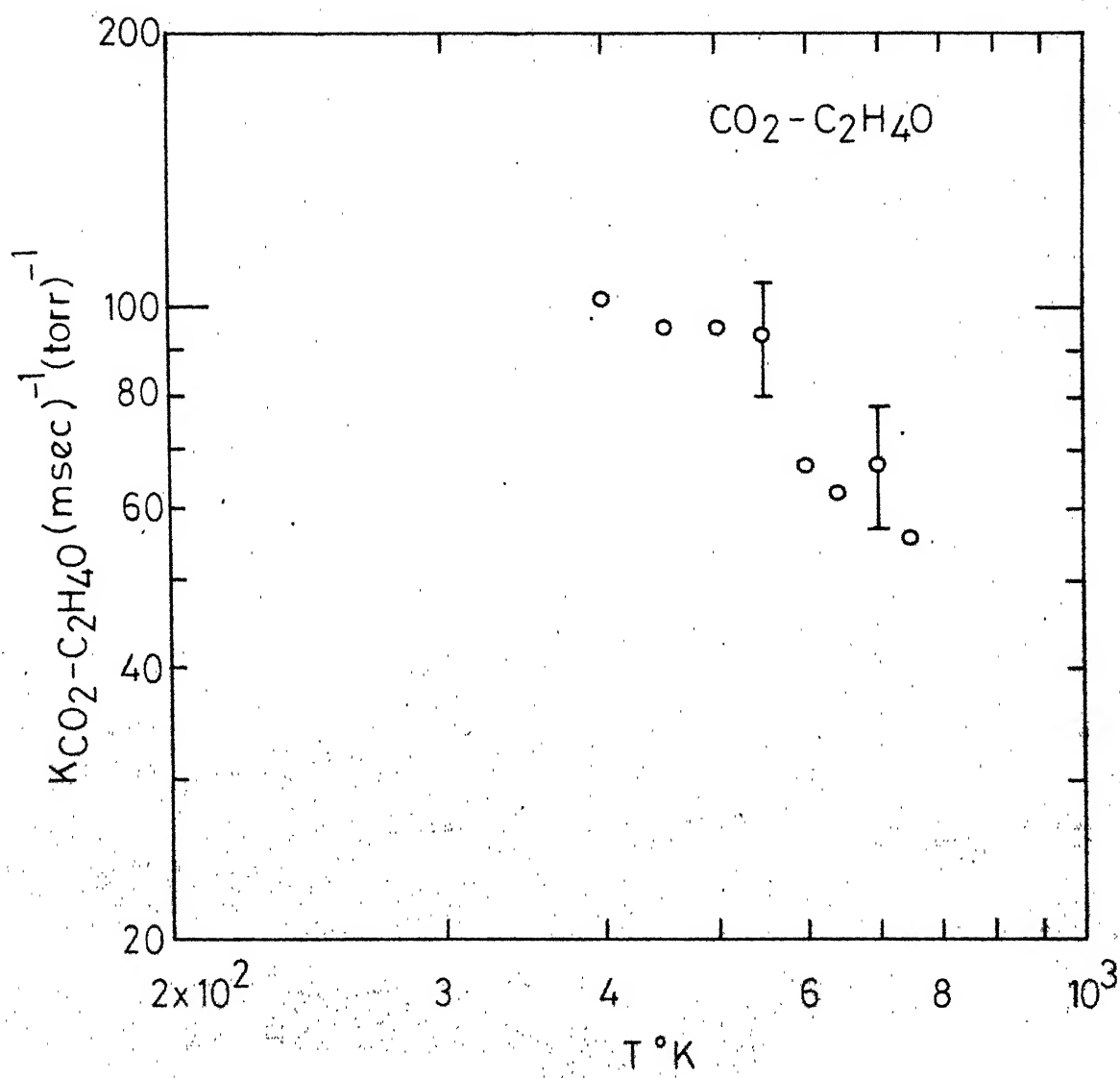
Fig. 10 – Temperature dependence of $K_{CO_2-C_2H_4O}$

## TABLE 3A

TEMPERATURE (K)= 650.0          CARBONDIOXIDE-ETHYLENEOXIDE

(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.112 | | X = 0.075 | | X = 0.026 | |
|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 13.4 | 114.0 | 13.8 | 82.2 | 19.8 | 92.9 |
| 13.4 | 109.8 | 13.8 | 92.5 | 19.8 | 78.7 |
| 12.1 | 92.5 | 12.3 | 84.9 | 17.8 | 69.9 |
| 12.1 | 115.3 | 12.3 | 90.4 | 17.8 | 78.2 |
| 10.8 | 113.6 | 11.2 | 67.5 | 16.0 | 66.6 |
| 10.3 | 99.7 | 11.2 | 62.8 | 16.0 | 65.8 |
| 9.5 | 96.1 | 10.1 | 66.9 | 14.0 | 70.1 |
| 9.5 | 92.9 | 10.1 | 68.3 | 14.0 | 55.9 |
| 8.4 | 66.3 | 8.7 | 57.4 | 11.5 | 44.2 |
| 3.4 | 74.7 | 8.7 | 61.4 | 11.5 | 53.2 |
| 7.1 | 65.7 | 7.7 | 49.6 | 11.5 | 40.8 |
| 7.1 | 53.1 | 7.7 | 56.6 | 9.9 | 53.7 |
| 6.1 | 64.1 | 6.4 | 47.4 | 9.9 | 38.5 |
| 6.1 | 61.4 | 6.4 | 49.0 | 8.0 | 34.2 |
| 5.0 | 48.5 | 5.2 | 41.4 | 8.0 | 37.1 |
| 5.0 | 39.9 | 5.2 | 39.2 | 6.2 | 32.3 |
| 5.0 | 50.4 | 4.2 | 30.7 | 6.2 | 30.0 |
| 3.7 | 38.7 | 4.2 | 29.1 | 2.5 | 16.8 |
| 3.7 | 40.7 | 2.8 | 24.0 | 4.3 | 41.7 |
| 2.5 | 31.6 | 2.8 | 25.2 | 2.5 | 27.6 |
| 2.5 | 29.6 | | | 2.5 | 22.5 |

K(OBS)= 8.04±0.01          K(OBS)= 5.84±0.02          K(OBS)= 3.92±0.04

K(CO2-C2H4O)= 55.5 ± 7.3(MILLISEC.TORR)

## TABLE 23

CARBONDIOXIDE-ETHYLENEOXIDE

TEMPERATURE (K)= 540.0
(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.027 | | X = 0.051 | | X = 0.079 | | X = 0.115 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 22.8 | 53.7 | 22.7 | 92.1 | 19.8 | 102.5 | 19.5 | 172.0 |
| 22.8 | 49.1 | 19.9 | 78.2 | 19.8 | 109.8 | 18.2 | 146.0 |
| 19.8 | 44.7 | 17.5 | 71.9 | 17.0 | 117.0 | 18.2 | 150.5 |
| 19.8 | 45.5 | 17.5 | 63.4 | 17.0 | 104.0 | 15.3 | 131.8 |
| 17.4 | 41.4 | 15.9 | 55.5 | 14.8 | 85.4 | 12.8 | 94.5 |
| 17.4 | 41.8 | 15.9 | 56.4 | 14.8 | 84.4 | 12.8 | 103.7 |
| 17.4 | 41.7 | 12.7 | 52.1 | 13.0 | 77.0 | 11.1 | 98.5 |
| 16.3 | 42.4 | 12.7 | 53.3 | 13.0 | 79.1 | 11.1 | 87.5 |
| 16.3 | 46.4 | 11.2 | 49.4 | 10.9 | 61.4 | 9.7 | 74.7 |
| 14.5 | 36.0 | 11.2 | 42.2 | 10.9 | 70.0 | 9.7 | 68.0 |
| 14.5 | 35.8 | 9.1 | 28.8 | 8.2 | 51.5 | 8.0 | 60.5 |
| 12.4 | 43.3 | 9.1 | 40.4 | 8.2 | 48.4 | 6.5 | 57.9 |
| 12.4 | 39.0 | 7.4 | 33.4 | 6.5 | 40.0 | 6.6 | 55.3 |
| 10.8 | 34.4 | 7.4 | 32.7 | 6.5 | 38.3 | 4.3 | 42.8 |
| 10.6 | 31.2 | 5.6 | 20.8 | 4.6 | 26.3 | 4.3 | 36.3 |
| 7.4 | 28.8 | 5.6 | 30.0 | 4.6 | 28.8 | 3.2 | 38.0 |
| 7.4 | 26.6 | 4.2 | 21.8 | 3.0 | 21.8 | 3.2 | 41.0 |
| 5.3 | 18.5 | 4.2 | 21.5 | 3.0 | 26.2 | 4.4 | 45.4 |
| 5.3 | 19.1 | 4.2 | 23.2 | 3.3 | 34.5 | 3.4 | 45.9 |
| 3.6 | 16.8 | 3.0 | 22.6 | 2.8 | 25.3 | 3.4 | 49.0 |
| 3.6 | 14.2 | 3.0 | 22.1 | 2.8 | 20.7 | 2.4 | 32.9 |
| 4.0 | 16.8 | | | | | 2.4 | 34.1 |

K(OBS)= 1.78±0.07    K(OBS)= 3.55±0.05    K(OBS)= 5.51±0.09    K(OBS)= 7.90±0.25

K(CO2-C2H4O)= 52.5 ± 7.2(MILLISEC.TORR)$^{-1}$

## TABLE 24

TEMPERATURE (K)= 500.0  CARBONDIOXIDE-ETHYLENEOXIDE
(PRESSURE (P) IN TORR AND TOW INVERSE $(\tau^{-1})$ IN INVERSE MILLISEC.)

| X = 0.027 | | X = 0.051 | | X = 0.079 | | X = 0.115 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 24.2 | 90.2 | 22.4 | 151.0 | 20.4 | 126.0 | 16.5 | 150.0 |
| 24.2 | 75.6 | 22.4 | 147.0 | 20.4 | 117.8 | 16.5 | 165.0 |
| 22.8 | 69.7 | 19.2 | 102.2 | 17.5 | 10.0 | 14.3 | 154.0 |
| 22.0 | 76.4 | 19.2 | 103.2 | 17.5 | 06.0 | 14.3 | 140.1 |
| 19.8 | 76.3 | 16.8 | 109.5 | 15.9 | 12.0 | 12.7 | 124.5 |
| 19.0 | 70.6 | 16.8 | 107.8 | 15.9 | 94.2 | 12.7 | 136.2 |
| 15.9 | 58.3 | 15.3 | 87.3 | 13.1 | 76.6 | 10.6 | 112.3 |
| 15.9 | 61.8 | 15.3 | 66.0 | 11.0 | 82.2 | 10.6 | 104.7 |
| 13.8 | 48.8 | 13.0 | 78.9 | 11.0 | 82.3 | 9.6 | 103.2 |
| 13.8 | 65.8 | 11.2 | 75.3 | 9.2 | 58.7 | 9.6 | 107.5 |
| 11.9 | 40.4 | 9.2 | 55.0 | 9.2 | 72.2 | 8.6 | 96.3 |
| 11.7 | 43.2 | 9.2 | 63.4 | 8.7 | 62.2 | 8.6 | 98.8 |
| 9.5 | 43.4 | 7.4 | 57.2 | 8.6 | 64.3 | 6.5 | 83.0 |
| 9.5 | 44.4 | 7.4 | 53.8 | 5.8 | 50.0 | 6.5 | 81.0 |
| 6.4 | 24.4 | 5.8 | 38.8 | 5.8 | 48.6 | 6.2 | 63.3 |
| 6.4 | 32.5 | 5.8 | 45.0 | 4.8 | 38.5 | 6.2 | 68.5 |
| 5.1 | 22.9 | 3.8 | 36.3 | 4.8 | 37.5 | 4.4 | 46.6 |
| 5.1 | 27.2 | 3.8 | 32.3 | 3.3 | 35.1 | 4.4 | 45.4 |
| 4.0 | 24.6 | 4.4 | 26.2 | 3.3 | 34.5 | 3.4 | 45.9 |
| 4.0 | 25.6 | 3.0 | 22.6 | 2.8 | 25.3 | 3.4 | 49.0 |
| 4.0 | 24.7 | 3.0 | 22.1 | 2.8 | 20.7 | 2.4 | 32.9 |
| 4.0 | 16.8 | | | | | 2.4 | 34.1 |

K(OBS)= 2.95±0.09    K(OBS)= 5.58±0.02    K(OBS)= 5.20±0.01    K(OBS)= 8.97±0.07

K(CO2-C2H4O)= 67. ± 16.5(MILLISEC.TORR)$^{-1}$

## TABLE 26

CARBONDIOXIDE-ETHYLENEOXIDE

TEMPERATURE (K)= 450.0
(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.027 | | X = 0.051 | | X = 0.079 | | X = 0.115 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 19.7 | 68.7 | 20.1 | 94.5 | 19.4 | 174.0 | 18.8 | 202.0 |
| 19.7 | 69.5 | 18.6 | 84.5 | 16.3 | 140.0 | 18.9 | 222.0 |
| 17.9 | 57.8 | 18.6 | 87.5 | 16.3 | 133.5 | 16.5 | 183.8 |
| 16.2 | 56.6 | 16.2 | 80.0 | 16.3 | 120.4 | 16.5 | 172.5 |
| 16.2 | 56.8 | 16.2 | 73.0 | 12.3 | 107.2 | 14.1 | 144.3 |
| 14.0 | 52.6 | 15.1 | 76.0 | 12.3 | 98.5 | 14.1 | 166.9 |
| 14.0 | 48.7 | 15.1 | 77.6 | 11.2 | 93.2 | 9.8 | 108.7 |
| 12.2 | 53.5 | 13.6 | 71.4 | 11.2 | 95.9 | 8.0 | 78.0 |
| 12.2 | 43.1 | 13.6 | 69.8 | 10.0 | 90.6 | 8.0 | 76.4 |
| 10.6 | 39.9 | 12.4 | 61.0 | 10.0 | 90.6 | 6.7 | 71.3 |
| 10.6 | 37.7 | 12.4 | 65.4 | 8.3 | 90.4 | 6.7 | 71.4 |
| 10.6 | 39.0 | 9.8 | 52.7 | 3.3 | 79.6 | 5.0 | 47.7 |
| 3.2 | 27.4 | 9.8 | 52.7 | 7.0 | 48.4 | 5.0 | 53.0 |
| 8.2 | 31.3 | 8.2 | 50.9 | 7.0 | 47.9 | 4.3 | 45.4 |
| 6.6 | 28.4 | 8.2 | 52.0 | 6.0 | 48.5 | 4.3 | 47.9 |
| 6.6 | 28.8 | 5.9 | 43.5 | 6.0 | 46.2 | 3.0 | 40.4 |
| 4.7 | 19.4 | 5.9 | 42.4 | 4.0 | 34.0 | 3.0 | 46.4 |
| 4.7 | 21.6 | 4.4 | 32.7 | 4.0 | 36.8 | 4.7 | 22.3 |
| 3.1 | 20.0 | 4.4 | 26.2 | 2.8 | 29.6 | 4.7 | 28.7 |
| 3.0 | 62.7 | 3.0 | 22.6 | 2.8 | 25.3 | 3.6 | 52.7 |
| 2.5 | 29.6 | 3.0 | 22.1 | 2.8 | 20.7 | 2.4 | 32.9 |
| | | | | | | 2.4 | 34.1 |

K(OBS)= 3.05±0.06   K(OBS)= 4.01±0.08   K(OBS)= 8.37±0.08   K(OBS)= 11.04±0.32

K(CO2-C2H4O)= 93.5 ± 12.(MILLISEC.TORR)$^{-1}$

## TABLE 26

TEMPERATURE (K)= 400.0     CARBONDIOXIDE-ETHYLENEOXIDE

(PRESSURE (P) IN TORR AND TOMINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.115 | | X = 0.079 | | X = 0.051 | | X = 0.027 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 16.3 | 204.0 | 18.9 | 164.5 | 17.2 | 122.0 | 22.1 | 99.0 |
| 16.3 | 196.0 | 18.9 | 160.5 | 17.2 | 131.7 | 22.1 | 85.6 |
| 13.4 | 174.0 | 16.6 | 149.0 | 15.8 | 118.0 | 18.5 | 81.7 |
| 13.4 | 192.5 | 16.6 | 146.5 | 15.8 | 126.0 | 16.2 | 63.7 |
| 10.2 | 131.0 | 13.4 | 112.4 | 12.6 | 92.5 | 16.2 | 66.5 |
| 10.2 | 154.0 | 13.4 | 107.0 | 12.6 | 95.4 | 15.6 | 63.3 |
| 9.2 | 111.0 | 11.6 | 100.5 | 11.3 | 79.8 | 15.6 | 69.6 |
| 7.8 | 100.0 | 11.6 | 126.8 | 11.3 | 76.2 | 12.8 | 60.2 |
| 7.8 | 94.0 | 8.8 | 94.0 | 9.5 | 49.8 | 12.0 | 55.8 |
| 6.6 | 92.0 | 8.8 | 91.5 | 9.5 | 59.8 | 11.0 | 59.2 |
| 6.6 | 89.6 | 7.4 | 85.4 | 7.6 | 44.6 | 11.0 | 53.5 |
| 5.1 | 74.6 | 7.4 | 71.8 | 7.6 | 46.8 | 10.0 | 44.8 |
| 4.5 | 77.5 | 6.2 | 65.0 | 6.8 | 48.3 | 10.0 | 49.5 |
| 4.6 | 72.4 | 6.2 | 73.3 | 6.8 | 54.5 | 8.0 | 45.1 |
| 4.0 | 51.0 | 6.2 | 45.2 | 6.0 | 44.8 | 8.0 | 29.1 |
| 4.0 | 52.7 | 6.2 | 45.0 | 6.0 | 44.9 | 5.8 | 26.7 |
| 3.4 | 48.8 | 4.6 | 50.2 | 5.1 | 36.8 | 5.3 | 32.9 |
| 3.4 | 48.3 | 4.6 | 64.4 | 5.1 | 37.2 | 4.7 | 22.3 |
| 3.0 | 61.8 | 2.5 | 40.6 | 2.7 | 30.1 | 4.7 | 28.7 |
| 3.0 | 62.7 | 2.5 | 39.1 | 2.7 | 33.2 | 3.6 | 52.7 |
| 2.5 | 29.6 | | | 2.5 | 22.3 | 2.4 | 32.9 |
| | | | | | | 2.4 | 34.1 |

K(OBS)= 11.79±0.30     K(OBS)= 7.60±0.03     K(OBS)= 7.21±0.30     K(OBS)= 3.79±0.04

K(CO2-C2H4O)= 94.9 ± 17.(MILLISEC.TORR)$^{-1}$

## TABLE 27

TEMPERATURE (K) = 250.0

(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

CARBONDIOXIDE-ETHYLENEOXIDE

| X = 0.027 | | X = 0.051 | | X = 0.079 | | X = 0.115 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 22.1 | 93.2 | 18.2 | 124.5 | 16.3 | 154.0 | 12.7 | 136.3 |
| 22.1 | 89.5 | 18.2 | 126.0 | 16.3 | 170.0 | 12.7 | 151.7 |
| 19.8 | 80.7 | 15.8 | 112.2 | 13.2 | 128.5 | 11.9 | 144.0 |
| 19.8 | 88.7 | 15.8 | 110.0 | 13.2 | 138.1 | 11.9 | 134.8 |
| 15.8 | 57.8 | 14.2 | 94.5 | 11.2 | 115.8 | 11.0 | 161.5 |
| 15.8 | 62.9 | 14.2 | 92.6 | 11.2 | 125.0 | 11.0 | 115.0 |
| 15.9 | 50.0 | 12.6 | 76.6 | 9.6 | 84.7 | 9.9 | 124.2 |
| 14.2 | 54.5 | 12.6 | 82.5 | 9.6 | 34.0 | 9.9 | 121.5 |
| 14.2 | 48.4 | 10.8 | 79.4 | 8.1 | 71.0 | 8.4 | 119.0 |
| 10.2 | 42.7 | 10.8 | 78.6 | 8.1 | 81.5 | 8.4 | 114.3 |
| 10.2 | 37.4 | 8.6 | 58.9 | 7.2 | 69.4 | 6.9 | 79.6 |
| 8.4 | 37.2 | 8.6 | 65.0 | 7.2 | 65.6 | 6.9 | 94.3 |
| 8.4 | 33.? | 7.2 | 53.8 | 5.6 | 53.5 | 6.0 | 89.4 |
| 6.9 | 37.4 | 7.2 | 61.8 | 5.6 | 50.8 | 6.0 | 88.0 |
| 6.9 | 30.7 | 5.9 | 40.7 | 4.3 | 43.1 | 5.3 | 87.5 |
| 5.8 | 27.4 | 5.9 | 44.2 | 4.3 | 34.5 | 5.3 | 76.6 |
| 5.8 | 20.2 | 4.0 | 52.7 | 3.1 | 37.0 | 4.2 | 56.6 |
| 4.7 | 22.3 | 4.0 | 30.9 | 3.1 | 36.0 | 4.2 | 59.6 |
| 4.7 | 20.6 | 2.7 | 21.6 | 4.3 | 41.7 | 3.6 | 58.4 |
| 3.2 | 25.0 | 2.7 | 27.1 | 2.5 | 27.6 | 3.6 | 52.7 |
| 3.2 | 29.6 | | | 2.5 | 22.3 | 2.4 | 32.9 |
| 2.5 | | | | | | 2.4 | 34.1 |

K(OBS) = 3.69±0.10    K(OBS) = 6.39±0.06    K(OBS) = 10.13±0.20    K(OBS) = 10.57±0.24

$K(CO_2-C_2H_4O)$ = 94.7 ± 22.(MILLISEC.TORR)$^{-1}$

## TABLE 28

TEMPERATURE (K)= 301.8    CARBONDYOXIDE-ETHYLENEOXYDE

(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.079 | | X = 0.115 | | X = 0.051 | | X = 0.027 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 14.9 | 168.0 | 16.8 | 203.5 | 15.5 | 167.0 | 20.0 | 92.0 |
| 14.5 | 117.0 | 16.8 | 247.0 | 15.5 | 174.5 | 20.0 | 93.5 |
| 14.0 | 131.0 | 11.5 | 180.0 | 14.0 | 148.5 | 18.2 | 99.5 |
| 14.0 | 131.0 | 11.5 | 173.0 | 14.0 | 143.0 | 17.6 | 85.3 |
| 12.8 | 131.0 | 9.1 | 149.0 | 12.2 | 139.0 | 17.5 | 86.7 |
| 12.9 | 133.0 | 9.1 | 149.0 | 10.8 | 95.0 | 13.7 | 75.2 |
| 12.9 | 122.3 | 8.0 | 135.0 | 10.8 | 102.5 | 13.7 | 70.8 |
| 10.9 | 107.0 | 8.0 | 139.5 | 8.0 | 91.7 | 11.1 | 57.2 |
| 10.5 | 121.4 | 6.0 | 106.5 | 9.0 | 101.0 | 9.2 | 49.3 |
| 10.5 | 101.0 | 5.6 | 68.0 | 7.0 | 90.3 | 7.9 | 43.2 |
| 10.2 | 108.0 | 5.6 | 89.0 | 7.0 | 81.4 | 7.3 | 55.6 |
| 10.2 | 81.0 | 4.0 | 81.0 | 6.2 | 75.3 | 6.4 | 35.7 |
| 7.4 | 89.0 | 4.0 | 85.6 | 6.2 | 34.8 | 6.4 | 56.0 |
| 7.4 | 72.0 | 3.8 | 69.5 | 5.0 | 60.3 | 4.2 | 27.5 |
| 7.2 | 101.0 | 3.8 | 66.3 | 5.0 | 61.7 | 4.2 | 31.3 |
| 7.2 | 56.6 | 2.2 | 53.0 | 4.0 | 61.0 | 3.0 | 36.8 |
| 5.0 | 56.6 | 2.2 | 49.7 | 4.0 | 60.5 | 3.0 | 34.4 |
| 5.0 | 45.3 | 4.2 | 21.5 | 3.0 | 45.8 | 2.9 | 32.3 |
| 3.4 | 46.9 | 4.2 | 23.2 | 3.0 | 46.4 | 3.4 | 45.9 |
| 3.4 | 41.5 | 3.0 | 22.6 | 2.8 | 25.3 | 3.4 | 49.0 |
| 2.6 | 41.3 | 3.0 | 22.1 | 2.8 | 20.7 | 2.4 | 32.9 |
| 2.5 | 37.8 | | | | | 2.4 | 34.1 |

K(OBS)= 6.58±0.06    K(OBS)= 12.25±0.19    K(OBS)= 9.21±0.01    K(OBS)= 3.82±0.03

K(CO2-C2H4O)= 101 ± 31    (MILLISEC.TORR)$^{-1}$

Table 29

Rate constants, cross-sections and probabilities of energy transfer from $CO_2(00°1)$ to $C_2H_4O$

| T°K | $K_{CO_2-M}(ms^{-1}torr^{-1})$ | $\sigma \overset{o}{A}^2$ | $P_{exp} \times 10^2$ |
|---|---|---|---|
| 301 | 101 ± 31 | 0.59 ± 0.18 | 1.08 ± 0.33 |
| 350 | 94.7± 22.4 | 0.59 ± 0.14 | 1.09 ± 0.33 |
| 400 | 94.9± 17.7 | 0.64 ± 0.12 | 1.17 ± 0.26 |
| 450 | 93.5± 12.8 | 0.67 ± 0.09 | 1.22 ± 0.22 |
| 500 | 67.0± 16.5 | 0.502 ± 0.13 | 0.92 ± 0.17 |
| 540 | 62.5± 7.2 | 0.49 ± 0.06 | 0.90 ± 0.23 |
| 600 | 67.2± 10.4 | 0.552 ± 0.08 | 1.01 ± 0.1 |
| 650 | 55.5± 7.3 | 0.47 ± 0.06 | 0.87 ± 0.16 |

INTERPRETATION OF RESULTS

Ethylene oxide is also an efficient collision partner with a rate comparable to that of Methanol-d. Such high energy transfer rates and their decrease with increasing temperature suggest that near-resonant V-V energy transfer processes are of primary importance in the deactivation of the $CO_2(00°1)$ mode. Following the vibrational assignments of Lord and Nolin[57] and Thompson and Cave[58] for Ethylene oxide molecule the following processes need to be considered.

$$CO_2(00°1) + C_2H_4O(0) \longrightarrow CO_2(0) + C_2H_4O(\mathcal{J}=2312)+\triangle E = 37 \text{ cm}^{-1} \qquad 4.21$$

$$\longrightarrow CO_2(0) + C_2H_4O(\mathcal{J}=2394)+\triangle E =-45 \text{ cm}^{-1} \qquad 4.22$$

$$\longrightarrow CO_2(0) + C_2H_4O(\mathcal{J}=2269)+\triangle E = 80 \text{ cm}^{-1} \qquad 4.23$$

$$\longrightarrow CO_2(0) + C_2H_4O(\mathcal{J}=2451)+\triangle E =-102 \text{ cm}^{-1} \qquad 4.24$$

$$\longrightarrow CO_2(100)+C_2H_4O(\mathcal{J}_5=877)+\triangle E = 83 \text{ cm}^{-1} \qquad 4.25$$

$$\longrightarrow CO_2(100)+C_2H_4O(\mathcal{J}_{12}=892)+\triangle E = 68 \text{ cm}^{-1} \qquad 4.26$$
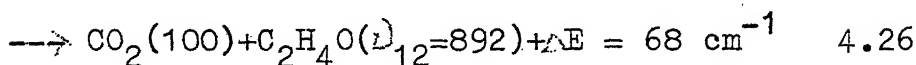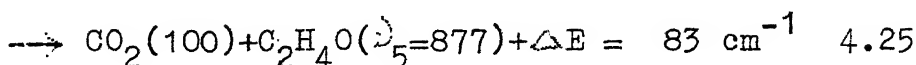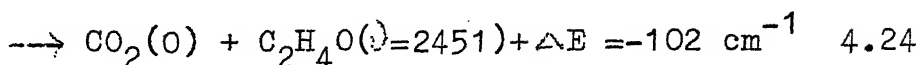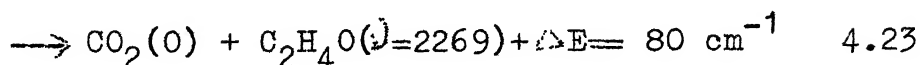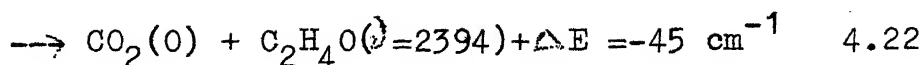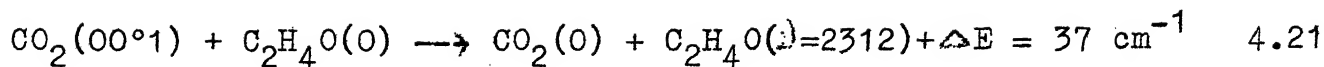
The transitions in $C_2H_4O$ in the first four processes (ie. equations 4.21 - 4.24) are weak whereas those in processes 4.25 and 4.26 are very strong.

## PROBABILITY CALCULATIONS

The dipole moments of Ethylene oxide transitions for none of the above processes are available. The energy transfer probabilities for all the above processes are calculated using SB theory where only the dipole-dipole interactions are assumed to contribute and are presented in Table 30. It is assumed that Ethylene oxide may be approximated by an oblate symmetric top molecule and the molecular constants used are given in Table 5. A close look at the probabilities in Table 30 reveals that the probabilities decrease with increasing temperature for processes 4.21 and 4.22 where $\triangle E$ is 37 and -45 $\text{cm}^{-1}$ respectively,

Table 30

Calculated Energy Transfer probabilities* for different processes of $CO_2-C_2H_4O$ system

| T°K | $p_{21}\times10^{35}$ | $p_{22}\times10^{35}$ | $p_{23}\times10^{35}$ | $p_{24}\times10^{35}$ | $p_{25}\times10^{35}$ | $p_{26}\times10^{35}$ |
|---|---|---|---|---|---|---|
| 301 | 57.35 | 47.29 | 15.2 | 3.768 | 0.1836 | 0.3914 |
| 350 | 49.49 | 42.66 | 17.13 | 4.596 | 0.2105 | 0.4025 |
| 400 | 43.78 | 38.91 | 18.96 | 5.86 | 0.2373 | 0.4072 |
| 450 | 39.11 | 35.55 | 19.97 | 7.084 | 0.2543 | 0.4013 |
| 500 | 35.31 | 32.61 | 20.43 | 8.158 | 0.2638 | 0.3891 |
| 540 | 32.72 | 30.49 | 20.38 | 8.766 | 0.2656 | 0.3618 |
| 600 | 29.51 | 27.72 | 20.19 | 9.678 | 0.2664 | 0.3394 |
| 650 | 27.25 | 25.84 | 19.72 | 10.15 | 0.2623 | 0.3300 |

* Values are obtained by assuming unity for the unknown
transition dipole moments(squares) of M.

shows a broad maximum around 500°K for process 4.23 where $\triangle E$ is 80 cm$^{-1}$ and finally shows a positive temperature dependence as $\triangle E$ is further increased to 102 cm$^{-1}$ in process 4.24. The probability for process 4.24 increases by 3 times from 300 to 650°K whereas for processes 4.21 and 4.22 the decrease is by about a factor of two in the same temperature range. The experimentally derived probability for this system can be written as

$$P_{exp} = \sum_i a_i\, p_i + a_{25}\, p_{25} + a_{26}\, p_{26} \qquad 4.27$$

where the summation extends over the first four weak processes. It is a common practice to report the combined coefficients for weak bands[60]. Using a similar approach, equation 4.27 can be rewritten as

$$P_{exp} = a_{weak} \sum_i p_i + a(\nu_5 \longrightarrow 0)\, p_{25} + a(\nu_{12} \longrightarrow 0)\, p_{26} \qquad 4.28$$

The experimental probabilities at different temperatures are used to find out the dipole moment squares for the transition shown in processes 4.21 - 4.26. The values obtained using least squares analysis are

$$a_{weak} = 0.17 \times 10^{-39} esu^2 cm^2$$

$$a(\nu_5 \longrightarrow 0) = 0.66 \times 10^{-37} esu^2 cm^2$$

$$a(\nu_{12} \longrightarrow 0) = 1.8 \times 10^{-37} esu^2 cm^2$$

These values are in accordance with the relative spectroscopic absorption intensities[57,58]. Thus the calculated value, for the combined strength of the four bands which are reported to be weak, is about three orders of magnitude smaller than the very strong $\nu_{12} \longrightarrow 0$ transition. However, the values for $a(\nu_5 \longrightarrow 0)$ and $a(\nu_{12} \longrightarrow 0)$ are differing by a factor of about 2.3 even though both are reported to be very strong.

## $CO_2-CH_3CHO$
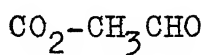
The deactivation of the $CO_2(00°1)$ mode in collisions with Acetaldehyde, whose molecular weight is the same as that of $CO_2$ and $C_2H_4O$ has been studied for different compositions in the temperature range of 300-650°K. In all the experimental runs the deactivation of this mode followed a single exponential decay which is deduced from the semilogarithmic plot of fluorescence signal intensity versus time. The deactivation rate constant $K_{CO_2-CH_3CHO}$ is deduced along the same lines as has been described previously and its temperature dependence is presented in Fig.11. The complete experimental data taken on this system is presented in Tables 31-36 at different temperatures. The collision cross-sections and the energy transfer probabilities calculated using equations 2.4 and 2.5 are presented in Table 37 along with the deactivation rate at different temperatures.
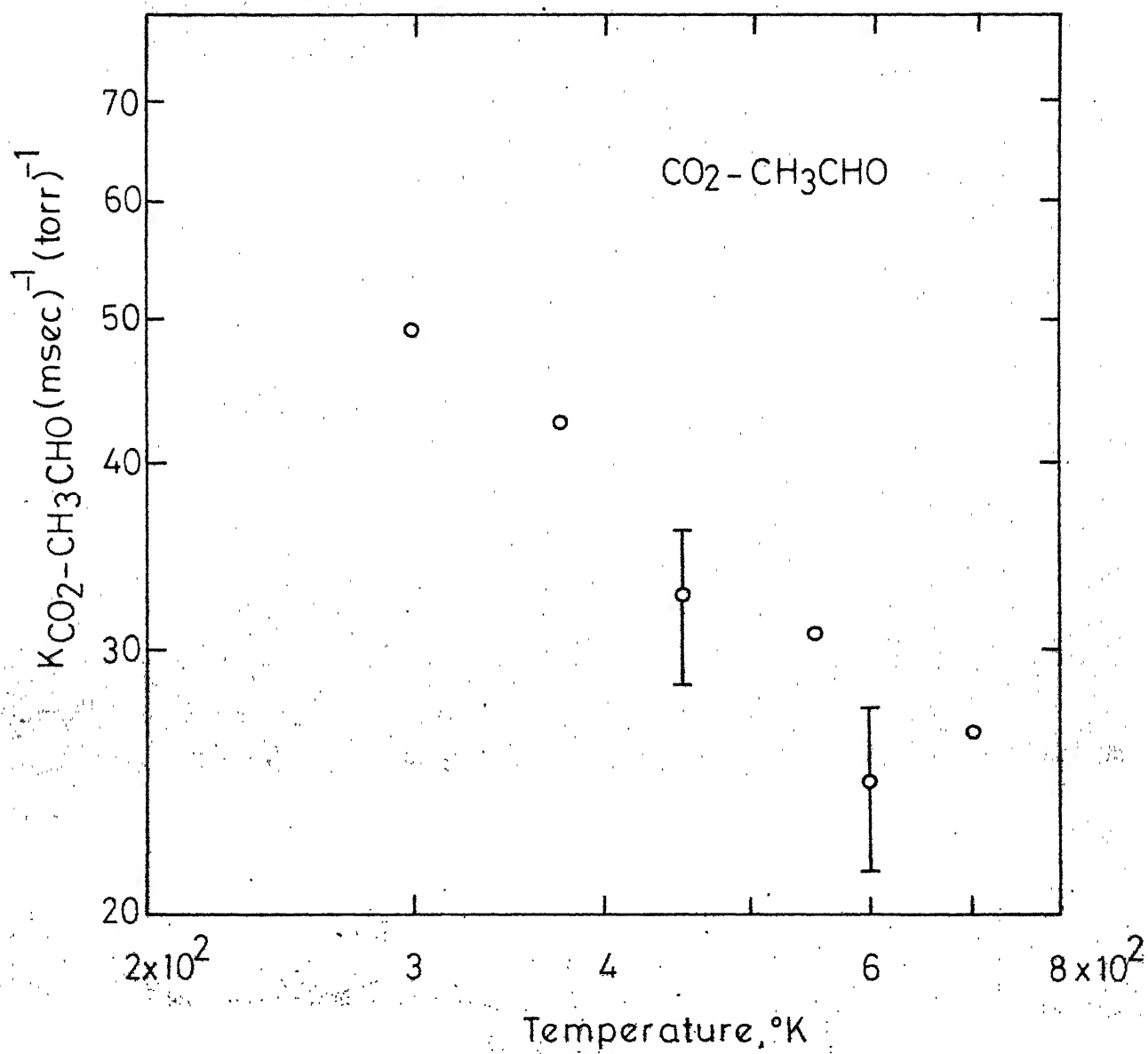
Fig 11 -Temperature dependence of $K_{CO_2-CH_3CHO}$

# TABLE 34

CARBON DIOXIDE-ACETALDEHYDE

TEMPERATURE (K) = 650.0.
(PRESSURE (P) IN TORR AND $\tau^{-1}$ INVERSE ($\tau^{-1}$) IN INVERSE MIL. ISEC.)

| X = 0.030 | | X = 0.059 | | X = 0.089 | | X = 3.113 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 24.1 | 69.9 | 16.2 | 55.0 | 14.4 | 69.4 | 16.3 | 91.4 |
| 18.8 | 61.1 | 15.2 | 55.5 | 14.4 | 59.4 | 16.3 | 72.2 |
| 18.9 | 53.3 | 14.1 | 50.1 | 12.8 | 52.5 | 13.5 | 64.9 |
| 15.3 | 50.0 | 12.3 | 45.9 | 12.3 | 57.1 | 11.3 | 60.9 |
| 14.4 | 50.1 | 12.3 | 40.7 | 11.5 | 52.9 | 11.3 | 61.7 |
| 12.8 | 45.9 | 10.6 | 34.3 | 10.1 | 41.8 | 11.3 | 50.1 |
| 12.8 | 40.0 | 9.4 | 35.4 | 10.1 | 41.5 | 11.0 | 61.9 |
| 11.2 | 36.7 | 9.4 | 35.0 | 9.5 | 37.4 | 11.0 | 61.9 |
| 11.2 | 48.2 | 7.8 | 23.4 | 8.5 | 44.0 | 9.4 | 47.9 |
| 9.4 | 34.0 | 7.8 | 28.3 | 8.6 | 39.7 | 9.4 | 52.8 |
| 9.4 | 34.1 | 5.2 | 24.2 | 7.0 | 32.3 | 7.3 | 39.4 |
| 7.7 | 29.8 | 5.2 | 30.5 | 7.0 | 30.1 | 7.3 | 40.5 |
| 7.7 | 28.8 | 5.2 | 33.4 | 6.1 | 25.4 | 6.5 | 37.8 |
| 6.3 | 27.4 | 4.8 | 28.7 | 5.1 | 24.4 | 5.5 | 34.9 |
| 6.3 | 25.4 | 4.9 | 25.5 | 5.1 | 25.5 | 4.7 | 23.3 |
| 4.3 | 23.6 | 3.7 | 19.3 | 4.9 | 24.1 | 4.7 | 23.9 |
| 4.8 | 24.8 | 3.7 | 19.9 | 4.9 | 24.6 | 3.3 | 23.3 |
| 4.8 | 26.6 | 2.2 | 15.2 | 3.4 | 24.6 | 3.3 | 20.4 |
| 3.2 | 16.9 | 2.2 | 15.2 | 3.4 | 22.2 | | |
| 3.2 | 15.2 | | | | | | |

K(OBS)= -2.50±0.07    K(OBS)= 2.54±0.02    <OBS>= 3.88±0.11    K(OBS)= 4.57±0.04

K(CO2-CH3CH3) = 26,5±4,9    (MILLISEC.TORR)$^{-1}$

## TABLE 32

TEMPERATURE (K)= 600.0      CARBONDIOXIDE-ACETALDEHYDE

(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.030 | | X = 0.059 | | X = 0.089 | | X = 0.113 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 23.4 | 63.2 | 21.8 | 62.1 | 17.5 | 80.8 | 16.2 | 70.2 |
| 23.4 | 57.3 | 21.8 | 70.1 | 17.5 | 73.0 | 16.2 | 69.0 |
| 21.0 | 60.8 | 18.4 | 64.9 | 13.8 | 52.5 | 14.4 | 64.7 |
| 21.0 | 54.8 | 17.0 | 51.6 | 13.8 | 47.5 | 14.4 | 72.2 |
| 19.4 | 47.1 | 17.0 | 50.9 | 11.6 | 54.6 | 12.9 | 67.8 |
| 19.4 | 51.5 | 14.7 | 47.8 | 11.6 | 51.8 | 12.8 | 63.7 |
| 16.9 | 52.9 | 14.7 | 51.8 | 10.0 | 44.7 | 11.4 | 52.2 |
| 16.9 | 42.2 | 14.7 | 54.4 | 10.0 | 52.1 | 11.4 | 57.3 |
| 14.9 | 40.4 | 13.4 | 44.0 | 8.6 | 42.6 | 11.4 | 57.0 |
| 14.9 | 47.4 | 13.4 | 47.8 | 8.6 | 38.2 | 9.8 | 45.9 |
| 12.5 | 37.7 | 12.1 | 39.9 | 8.6 | 33.8 | 9.8 | 44.8 |
| 12.5 | 46.4 | 12.1 | 41.3 | 7.0 | 38.8 | 8.6 | 44.5 |
| 10.2 | 32.6 | 10.2 | 37.8 | 7.0 | 29.1 | 8.5 | 45.7 |
| 10.2 | 31.5 | 10.2 | 39.4 | 7.0 | 27.3 | 7.4 | 36.1 |
| 7.7 | 26.5 | 6.6 | 30.1 | 5.3 | 23.3 | 7.4 | 44.7 |
| 7.7 | 27.8 | 6.6 | 32.3 | 5.3 | 22.2 | 6.1 | 37.7 |
| 7.7 | 26.1 | 4.3 | 19.7 | 3.3 | 23.3 | 6.1 | 32.7 |
| 5.5 | 23.1 | 4.3 | 21.1 | 3.3 | 24.3 | 4.6 | 27.2 |
| 5.5 | 21.3 | 2.6 | 16.9 | 1.8 | 16.3 | 4.6 | 29.0 |
| 3.7 | 16.9 | 2.6 | 17.3 | 1.8 | 15.4 | 3.0 | 22.4 |
| 3.7 | 17.1 | | | | | 3.0 | 20.8 |
| 3.7 | 16.8 | | | | | | |

K(OBS)= 2.20±0.02     K(OBS)= 2.58±0.01     K(OBS)= 3.67±0.03     K(OBS)= 3.90±0.04

K(CO2-CH3CHO)= 24.4±3.1    (MILLISEC.TORR)$^{-1}$

# TABLE 38

TEMPERATURE (K) = 525.0    CARBONDIOXIDE-ACETALDEHYDE

(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.030 | | X = 0.059 | | X = 0.089 | | X = 0.113 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 20.3 | 43.2 | 20.9 | 51.6 | 17.3 | 69.2 | 13.3 | 67.4 |
| 20.3 | 41.6 | 17.7 | 58.1 | 17.3 | 68.1 | 13.3 | 62.8 |
| 17.3 | 36.3 | 17.7 | 56.9 | 14.3 | 58.6 | 11.9 | 62.6 |
| 17.3 | 33.8 | 15.8 | 46.8 | 14.3 | 55.1 | 11.9 | 60.3 |
| 14.8 | 32.6 | 15.8 | 45.6 | 12.2 | 40.9 | 9.4 | 50.4 |
| 14.8 | 40.6 | 14.3 | 48.4 | 12.2 | 41.5 | 8.2 | 40.7 |
| 12.8 | 33.4 | 14.3 | 42.3 | 10.0 | 46.1 | 8.2 | 40.4 |
| 12.8 | 31.9 | 13.1 | 40.8 | 10.0 | 46.9 | 7.3 | 41.3 |
| 10.6 | 25.3 | 13.1 | 42.1 | 8.6 | 34.4 | 7.3 | 40.4 |
| 10.5 | 25.9 | 11.2 | 39.3 | 8.6 | 36.5 | 6.5 | 35.3 |
| 8.2 | 29.9 | 11.2 | 37.8 | 7.4 | 35.8 | 6.6 | 42.8 |
| 8.2 | 25.4 | 9.7 | 38.8 | 7.4 | 33.7 | 5.2 | 27.0 |
| 6.8 | 19.4 | 9.7 | 35.8 | 7.4 | 30.9 | 5.2 | 32.2 |
| 6.9 | 20.2 | 8.2 | 33.3 | 5.7 | 19.3 | 5.2 | 30.7 |
| 5.2 | 21.3 | 8.2 | 31.7 | 5.7 | 20.8 | 4.1 | 28.3 |
| 5.2 | 21.9 | 6.6 | 29.4 | 4.6 | 18.1 | 4.1 | 28.6 |
| 3.8 | 13.1 | 6.6 | 25.0 | 4.6 | 18.4 | 3.2 | 27.3 |
| 3.8 | 13.9 | 4.2 | 20.4 | 3.6 | 18.2 | 3.2 | 25.0 |
| 5.5 | 21.3 | 4.2 | 22.4 | 3.6 | 17.9 | 4.6 | 29.0 |
| 3.7 | 16.9 | 2.6 | 17.3 | 2.5 | 14.0 | 3.0 | 22.4 |
| 3.7 | 17.1 | | | 2.5 | 14.0 | 3.0 | 20.8 |
| 3.7 | 16.8 | | | | | | |

K(OBS) = 1.55±0.06    K(OBS)= 2.15±0.02    K(OBS)= 3.69±0.03    K(OBS)= 4.09±0.04

K(CO2-CH3CHD)= 30.9±5.    (MILLISEC.TORR)$^{-1}$

## TABLE 340

CARBONDIOXIDE-ACETALDEHYDE

TEMPERATURE (K)= 450.0

(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.030 | | X = 0.059 | | X = 0.089 | | X = 0.113 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 25.2 | 53.0 | 20.2 | 69.9 | 20.2 | 81.4 | 12.6 | 58.6 |
| 25.2 | 48.1 | 17.7 | 53.7 | 15.4 | 62.2 | 12.5 | 56.2 |
| 21.1 | 40.9 | 15.2 | 50.9 | 15.4 | 62.5 | 10.7 | 55.9 |
| 21.1 | 40.9 | 15.2 | 52.9 | 13.0 | 57.1 | 10.7 | 57.6 |
| 18.6 | 37.4 | 13.0 | 49.1 | 9.9 | 49.4 | 9.2 | 53.3 |
| 18.5 | 41.2 | 11.4 | 39.3 | 9.9 | 46.1 | 9.2 | 49.6 |
| 15.8 | 35.2 | 11.4 | 39.1 | 9.9 | 50.5 | 7.4 | 41.4 |
| 15.6 | 35.5 | 9.9 | 31.9 | 8.5 | 42.9 | 7.4 | 42.7 |
| 13.6 | 31.7 | 9.9 | 34.7 | 8.5 | 37.0 | 5.9 | 33.9 |
| 13.6 | 32.6 | 8.4 | 38.4 | 6.6 | 30.1 | 5.9 | 39.9 |
| 12.0 | 30.7 | 8.4 | 39.5 | 6.6 | 30.6 | 4.5 | 29.1 |
| 12.0 | 33.4 | 6.6 | 27.0 | 5.6 | 28.8 | 4.6 | 30.6 |
| 10.2 | 26.5 | 6.6 | 27.4 | 5.6 | 28.8 | 3.7 | 22.8 |
| 10.2 | 28.3 | 5.6 | 24.5 | 4.3 | 24.3 | 3.7 | 25.4 |
| 8.3 | 22.9 | 5.6 | 24.2 | 4.3 | 23.5 | 3.0 | 21.2 |
| 8.3 | 22.9 | 3.6 | 18.6 | 3.0 | 18.5 | 3.0 | 23.0 |
| 6.6 | 23.6 | 3.6 | 19.7 | 3.0 | 20.7 | 3.2 | 27.3 |
| 6.5 | 21.1 | 4.2 | 20.4 | 3.6 | 18.2 | 3.2 | 25.0 |
| 4.5 | 17.1 | 4.2 | 22.4 | 3.6 | 17.9 | 4.5 | 29.0 |
| 4.5 | 16.0 | 2.6 | 17.3 | 2.5 | 14.0 | 3.0 | 22.4 |
| 3.7 | 17.1 | | | 2.5 | 14.0 | 3.0 | 20.8 |
| 3.7 | 16.8 | | | | | | |

K(OBS)= 1.51±0.04     K(OBS)= 2.80±0.01     K(OBS)= 3.63±0.02     K(OBS)= 4.04±0.02

K(CO2-CH3CHO)= 32.4±3.8   (MILLISEC.TORR)$^{-1}$

## TABLE 35A

### CARBONDIOXIDE-ACETALDEHYDE

TEMPERATURE (K)= 375.0
(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.030 | | X = 0.059 | | X = 0.089 | | X = 0.113 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 25.1 | 50.0 | 19.9 | 68.4 | 15.0 | 70.0 | 11.8 | 70.9 |
| 25.1 | 50.5 | 19.9 | 69.2 | 13.8 | 67.2 | 11.8 | 74.5 |
| 21.0 | 43.2 | 16.6 | 59.6 | 13.8 | 77.0 | 9.0 | 50.6 |
| 21.0 | 43.1 | 16.6 | 50.2 | 10.7 | 48.0 | 7.2 | 52.5 |
| 16.8 | 38.0 | 13.1 | 42.5 | 10.7 | 50.4 | 7.2 | 56.6 |
| 16.8 | 37.6 | 13.1 | 42.8 | 9.4 | 43.4 | 7.2 | 51.4 |
| 13.6 | 34.3 | 11.0 | 35.2 | 9.4 | 50.6 | 5.8 | 38.5 |
| 13.6 | 30.0 | 11.0 | 36.2 | 7.8 | 42.5 | 5.8 | 44.8 |
| 11.1 | 24.5 | 8.7 | 34.3 | 7.8 | 41.5 | 4.8 | 41.2 |
| 11.1 | 26.8 | 8.7 | 32.4 | 6.2 | 36.1 | 4.8 | 35.8 |
| 9.0 | 24.9 | 8.7 | 33.4 | 6.2 | 38.1 | 3.8 | 29.3 |
| 9.0 | 23.9 | 7.3 | 26.6 | 5.1 | 30.8 | 3.8 | 25.1 |
| 7.4 | 27.3 | 7.3 | 27.9 | 5.1 | 30.8 | 3.2 | 30.9 |
| 7.4 | 18.1 | 5.9 | 24.4 | 4.1 | 29.5 | 3.2 | 28.3 |
| 5.9 | 20.0 | 5.8 | 22.2 | 4.1 | 30.4 | 2.6 | 25.0 |
| 5.9 | 18.8 | 4.9 | 18.9 | 3.4 | 22.6 | 2.5 | 24.0 |
| 5.0 | 16.6 | 4.9 | 21.8 | 3.4 | 22.7 | 3.2 | 27.3 |
| 5.0 | 20.1 | 3.9 | 21.3 | 2.7 | 23.2 | 3.2 | 25.0 |
| 4.1 | 16.1 | 3.9 | 23.4 | 2.7 | 25.5 | 4.5 | 29.0 |
| 4.1 | 15.8 | 3.9 | 22.1 | 2.5 | 14.0 | 3.0 | 22.4 |
| 3.7 | 17.1 | 2.6 | 17.5 | 2.5 | 14.0 | 3.0 | 20.8 |
| 3.7 | 16.8 | 2.6 | 17.7 | | | | |

K(OBS)= 1.60±0.01    K(OBS)= 2.84±0.04    K(OBS)= 4.01±0.09    K(OBS)= 5.18±0.05

K(CO2-CH3CHO)= 42.4±1.2    (MILLISEC.TORR)$^{-1}$

## TABLE 36

### CARBONDIOXIDE-ACETALDEHYDE

TEMPERATURE (K)= 300.0
(PRESSURE (P) IN TORR AND TOMINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.030 | | X = 0.059 | | X = 0.089 | | X = 0.113 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 24.2 | 59.8 | 21.0 | 77.1 | 18.8 | 115.5 | 16.6 | 110.7 |
| 24.2 | 58.6 | 21.0 | 73.8 | 18.8 | 108.8 | 14.6 | 93.5 |
| 20.2 | 48.6 | 18.2 | 70.3 | 16.6 | 83.8 | 12.8 | 96.8 |
| 20.2 | 41.5 | 18.2 | 71.1 | 16.6 | 95.5 | 12.8 | 89.9 |
| 20.0 | 46.7 | 15.9 | 66.0 | 14.3 | 64.0 | 11.2 | 70.4 |
| 16.5 | 46.0 | 15.9 | 63.0 | 14.3 | 97.2 | 9.9 | 70.6 |
| 16.5 | 38.3 | 14.2 | 50.4 | 12.8 | 63.6 | 9.9 | 65.9 |
| 13.5 | 36.4 | 14.2 | 49.5 | 12.8 | 83.0 | 8.6 | 66.8 |
| 13.6 | 31.5 | 12.0 | 53.5 | 11.3 | 57.2 | 8.6 | 75.8 |
| 11.3 | 29.1 | 12.0 | 45.4 | 11.3 | 56.9 | 7.6 | 60.8 |
| 11.3 | 22.4 | 9.8 | 38.1 | 9.8 | 54.6 | 7.5 | 60.9 |
| 9.3 | 26.7 | 9.8 | 38.3 | 9.8 | 51.7 | 6.8 | 48.0 |
| 9.3 | 22.1 | 8.0 | 37.1 | 8.7 | 48.0 | 6.8 | 48.0 |
| 7.8 | 20.6 | 8.0 | 36.6 | 8.7 | 42.4 | 5.9 | 55.5 |
| 7.8 | 21.8 | 6.6 | 34.1 | 7.7 | 47.0 | 5.9 | 55.7 |
| 7.8 | 25.4 | 6.6 | 30.8 | 7.7 | 37.7 | 4.7 | 46.2 |
| 6.4 | 28.7 | 5.5 | 24.7 | 6.6 | 41.3 | 4.7 | 44.7 |
| 6.4 | 27.3 | 5.5 | 29.2 | 6.6 | 44.0 | 4.7 | 49.1 |
| 5.4 | 18.1 | 4.6 | 25.9 | 5.8 | 34.8 | 4.5 | 29.0 |
| 5.4 | 23.3 | 4.6 | 22.1 | 5.8 | 38.7 | 3.3 | 22.4 |
| 5.4 | 17.4 | 2.6 | 17.5 | 2.5 | 14.0 | 3.0 | 20.8 |
| 4.4 | 18.2 | 2.6 | 17.7 | | | | |
| 3.7 | 17.2 | | | | | | |
| 3.7 | 18.7 | | | | | | |

K(OBS)= 1.97±0.02    K(OBS)= 3.23±0.04    K(OBS)= 5.63±0.14    K(OBS)= 5.30±0.13
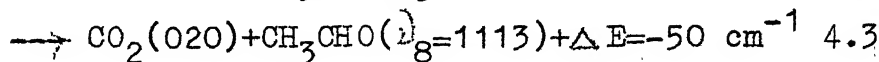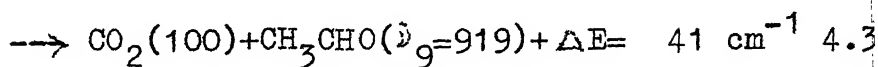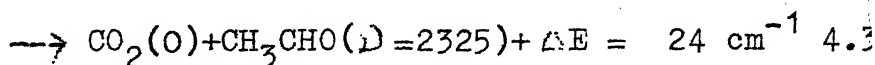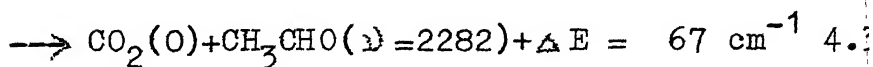
K(CO2-CH3CHO)= 48.6±10.7  (MILLISEC.TORR)⁻¹

Table 37

Rate constants, cross-sections and probabilities of energy transfer from $CO_2(00°1)$ to $CH_3CHO$

| $T°K$ | $K_{CO_2-M}(ms^{-1}torr^{-1})$ | $\sigma \, \overset{o}{A}^2$ | $P_{exp}x10^2$ |
|---|---|---|---|
| 301 | 48.6 ± 10.7 | 0.28 ± 0.06 | 0.61 ± 0.134 |
| 375 | 42.4 ± 1.2 | 0.28 ± 0.01 | 0.594 ± 0.017 |
| 450 | 32.4 ± 3.8 | 0.23 ± 0.03 | 0.498 ± 0.059 |
| 525 | 30.9 ± 5.0 | 0.23 ± 0.04 | 0.504 ± 0.083 |
| 600 | 24.4 ± 3.1 | 0.20 ± 0.03 | 0.432 ± 0.055 |
| 650 | 26.5 ± 4.9 | 0.23 ± 0.04 | 0.488 ± 0.091 |

## INTERPRETATION OF RESULTS

Among the seven molecules studied in the present work, Acetaldehyde is the least efficient in deactivating the $CO_2(00°1)$ mode by collisions. The deactivation rates decrease as the temperature is increased. The negative temperature dependence of the deactivation rates may be ascribed to near-resonant V-V energy transfer processes. Based on the vibrational frequencies, tabulated by Shimonouchi[40] for the fundamental bands, and those of Evans and Bernstein[61] and Morris[62] for mixed and over-tone bands, it appears that a number of processes ┌

contribute to the total deactivation rate. These are given below.

$$CO_2(00°1) + CH_3CHO(0) \longrightarrow CO_2(0)+CH_3CHO(\nu=2464)+\triangle E =-115 \text{ cm}^{-1} \quad 4.$$

$$\longrightarrow CO_2(0)+CH_3CHO(\nu=2218)+\triangle E = 131 \text{ cm}^{-1} \quad 4.$$

$$\longrightarrow CO_2(0)+CH_3CHO(\nu=2282)+\triangle E = 67 \text{ cm}^{-1} \quad 4.$$

$$\longrightarrow CO_2(0)+CH_3CHO(\nu=2325)+\triangle E = 24 \text{ cm}^{-1} \quad 4.3$$

$$\longrightarrow CO_2(100)+CH_3CHO(\nu_9=919)+\triangle E= 41 \text{ cm}^{-1} \quad 4.3$$

$$\longrightarrow CO_2(020)+CH_3CHO(\nu_8=1113)+\triangle E=-50 \text{ cm}^{-1} \quad 4.3$$
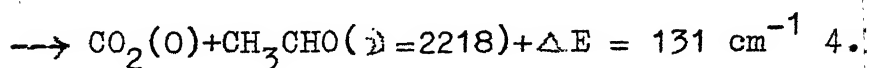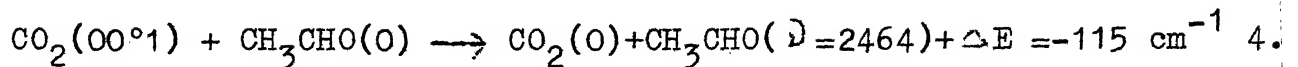
## PROBABILITY CALCULATIONS

The calculation of energy transfer probabilities using SB theory has been carried out at different temperatures for all the processes shown above. In these calculations it is assumed that the contribution due to dipole-dipole interactions is dominant and the proceedure followed to estimate the unknown transition moments is the same as before. The molecular constants used in these calculations are presented in Table 5 and Acetaldehyde molecule is approximated by a prolate symmetric top. The molecular diameter of $CH_3CHO$ is assumed to be the same as that of. $CH_3OH$ as is done by Stephenson[68]. The calculated probabilities are presented in Table 38. These probabilities show a negative temperature dependence for processes 4.32 and

Table 38

Calculated Energy Transfer probabilities* for different processes of $CO_2-CH_3CHO$ system

| $T^\circ K$ | $p_{29} \times 10^{-35}$ | $p_{30} \times 10^{-35}$ | $p_{31} \times 10^{-35}$ | $p_{32} \times 10^{-35}$ | $p_{33} \times 10^{-35}$ | $p_{34} \times 10^{-35}$ |
|---|---|---|---|---|---|---|
| 301 | 2.112 | 1.387 | 15.82 | 107.0 | 0.9502 | 0.3800 |
| 375 | 2.521 | 1.706 | 18.88 | 89.09 | 0.8892 | 0.4167 |
| 450 | 2.882 | 1.980 | 21.37 | 76.58 | 0.8179 | 0.4306 |
| 525 | 3.228 | 2.226 | 23.13 | 67.32 | 0.7504 | 0.4296 |
| 600 | 3.582 | 2.457 | 24.2 | 60.18 | 0.6902 | 0.42 |
| 650 | 3.871 | 2.636 | 21.37 | 56.51 | 0.6457 | 0.4138 |

* Values are obtained by assuming unity for the unknown
  transition dipole moments(squares) of M.

4.33 where $\Delta E$ is 24 and 41 $cm^{-1}$ respectively, exhibit a maximum at around 600°K and 450°K for processes 4.31 and 4.34 as $\Delta E$ is increased to 67 and -50 respectively and finally shows a positive temperature dependence as $\Delta E$ is further increased to -115 and 131 $cm^{-1}$ respectively for processes 4.29 and 4.30. No attempt has been made to estimate the contribution of short range forces to these processes. The experimentally derived probability for this system can be written as

$$P_{exp} = a_{weak} \sum_i p_i + a(\nu_9 \rightarrow 0) \, p_{33} + a(\nu_8 \rightarrow 0) \, p_{34} \qquad 4.35$$

The first four processes 4.29-4.32 involve weak transitions and their coefficients are combined as in the case of $C_2H_4O$. The three transition moments in 4.35 are then obtained by the least squares method. The values obtained are

$$a_{weak} = 0.3 \times 10^{-39} esu^2 cm^2$$

$$a(\nu_9 \rightarrow 0) = 0.15 \times 10^{-37} esu^2 cm^2$$

$$a(\nu_8 \rightarrow 0) = 0.21 \times 10^{-37} esu^2 cm^2$$

The relative magnitudes of these numbers are in accord with the spectroscopic observation[40,61,62] that $\nu_8 \rightarrow 0$ transition is strong, $\nu_9 \rightarrow 0$ is medium while the remaining four are weak.

## COMMENTS

All the three molecules $CO_2$, $C_2H_4O$ and $CH_3CHO$ have the same molecular weight. However, they differ considerably in their rate of deactivation of $CO_2(\nu_3)$, Ethylene oxide being two times more efficient than Acetaldehyde. The higher rate of deactivation by $C_2H_4O$ is due to the two very strong fundamental bands at 892 and 877 $cm^{-1}$ with high transition dipole moments. In Acetaldehyde, in addition to the four weak bands, the bands $\nu_8$ and $\nu_9$ designated as $CC$ stretch and $CH_3$ rock are responsible for the deactivation. The latter two are characterised as only strong and medium respectively. Thus, the transition dipole moment squares in Acetaldehyde are much smaller than that in Ethylene oxide and hence the lower rate compared to Ethylene oxide.

## $CO_2$-HCOOH

The rate of quenching of the $CO_2(00^\circ1)$ mode in collisions with Formic acid has been studied at three different temperatures namely 301, 350 and 400°K at different compositions. It should be noted that due to the large deactivation rates only mixtures with less than 1.5% at 301°K and less than 5% at 400°K could be studied. For all the experimental runs the fluorescence decay is observed to be a single exponential.

The data is analysed along the same lines as for the $CO_2$-$CH_3OH$ system. The complete experimental data on $CO_2$-HCOOH system is presented in Tables 39-41 at different temperatures. The temperature dependence of the deactivation rate constant $K_{CO_2-HCOOH}$ is shown in Fig.12. These rates along with the collision cross-sections and the energy transfer probabilities calculated using equations 2.4 and 2.5 are presented in Table 42 at different temperatures. However, it is shown below that because of dimer formation $K_{CO_2-HCOOH}$ obtained above can not be attributed to collisions between $CO_2$ and HCOOH.

Table 42

Rate constants, cross-sections and probabilities of energy transfer from $CO_2(00^\circ1)$ to HCOOH

| $T^\circ K$ | $K_{CO_2-M}(ms^{-1}torr^{-1})$ | $\overset{\circ}{A}{}^2$ | $P_{exp} \times 10^2$ |
|---|---|---|---|
| 301 | 336 ± 23 | 1.98 ± 0.14 | 3.52 ± 0.25 |
| 350 | 249 ± 50 | 1.58 ± 0.32 | 2.82 ± 0.56 |
| 400 | 140 ± 22 | 0.94 ± 0.15 | 1.69 ± 0.27 |

## TABLE 29

### CARBONDIOXIDE-FORMICACID

TEMPERATURE (K) = 400.0

(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.050 | | X = 0.025 | | X = 0.014 | | X = 0.005 | | X = 0.010 | |
|---|---|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 11.6 | 111.5 | 15.1 | 78.7 | 15.5 | 52.9 | 25.5 | 34.9 | 15.8 | 37.5 |
| 11.6 | 104.7 | 13.6 | 74.6 | 15.5 | 55.2 | 24.8 | 28.7 | 15.8 | 39.7 |
| 10.6 | 116.8 | 12.2 | 65.3 | 13.9 | 48.9 | 22.6 | 33.3 | 14.2 | 32.6 |
| 9.0 | 93.5 | 12.2 | 74.9 | 13.9 | 52.0 | 22.6 | 35.7 | 14.2 | 34.5 |
| 9.0 | 87.4 | 12.2 | 72.5 | 12.0 | 41.8 | 16.8 | 26.5 | 14.2 | 33.5 |
| 7.6 | 82.5 | 8.1 | 46.2 | 12.0 | 45.0 | 16.8 | 31.9 | 11.4 | 33.3 |
| 7.6 | 79.3 | 8.1 | 45.9 | 10.2 | 39.8 | 15.4 | 25.0 | 11.4 | 35.1 |
| 6.8 | 86.7 | 4.9 | 36.9 | 10.2 | 37.4 | 15.4 | 29.5 | 11.4 | 29.9 |
| 6.8 | 66.5 | 4.9 | 36.5 | 8.6 | 35.9 | 13.4 | 23.8 | 9.8 | 31.3 |
| 6.8 | 65.2 | 4.1 | 25.4 | 8.6 | 33.7 | 13.4 | 27.3 | 9.8 | 32.4 |
| 5.3 | 59.9 | 4.1 | 28.1 | 7.2 | 32.6 | 13.4 | 25.7 | 8.1 | 28.1 |
| 5.3 | 69.6 | 4.1 | 32.7 | 7.2 | 31.6 | 11.8 | 23.1 | 8.1 | 25.5 |
| 5.3 | 67.5 | 3.0 | 26.7 | 5.5 | 25.3 | 11.8 | 20.7 | 6.2 | 19.6 |
| 3.9 | 56.0 | 3.0 | 26.0 | 4.2 | 21.9 | 8.5 | 20.6 | 6.2 | 21.1 |
| 3.9 | 58.6 | 2.2 | 18.4 | 4.2 | 18.7 | 8.5 | 19.6 | 4.5 | 16.1 |
| 3.9 | 58.9 | 2.2 | 18.1 | 2.7 | 16.0 | 6.5 | 17.6 | 4.5 | 20.6 |
| 4.1 | 30.2 | 5.8 | 29.8 | 2.7 | 17.1 | 6.5 | 17.0 | 3.3 | 20.3 |
| 3.2 | 23.5 | 4.5 | 28.6 | 2.1 | 16.8 | 4.2 | 12.3 | 3.3 | 20.6 |
| 3.2 | 24.5 | 4.5 | 26.3 | 11.0 | 34.7 | 4.2 | 11.9 | 2.3 | 17.0 |
| 2.2 | 26.0 | 4.1 | 25.6 | 11.0 | 33.1 | | | 2.3 | 16.4 |
| 2.2 | 24.0 | 4.1 | 26.0 | 9.8 | 14.8 | | | 1.6 | 17.3 |
| | | 4.1 | 24.8 | 9.8 | 15.7 | | | 1.6 | 19.3 |
| | | 3.3 | 16.5 | 8.4 | 21.3 | | | | |
| | | 3.3 | 17.6 | 8.4 | 26.9 | | | | |
| | | | | 8.4 | 22.5 | | | | |

K(OBS) = 7.12±0.16  K(OBS) = 4.77±0.07  K(OBS) = 2.94±0.03  K(OBS) = 0.58±0.05  K(OBS) = 1.51±0.05

K(CO2-HCCOH) = 140±22.     (MILLISEC.TORR)$^{-1}$

EMPERATURE (K)= 350.0    CARBONDICXIDE-FORMICACID

(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

## TABLE 42

| X = 0.025 | | X = 0.014 | | X = 0.010 | | X = 0.005 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 13.6 | 105.4 | 17.9 | 68.3 | 16.4 | 47.8 | 16.4 | 35.2 |
| 13.6 | 106.6 | 17.9 | 60.4 | 16.4 | 52.6 | 16.4 | 34.7 |
| 12.7 | 95.4 | 15.9 | 56.0 | 12.2 | 39.2 | 15.3 | 30.9 |
| 12.7 | 98.1 | 14.4 | 50.2 | 12.2 | 42.8 | 15.3 | 30.2 |
| 10.7 | 92.0 | 14.4 | 56.1 | 12.2 | 34.1 | 13.8 | 28.4 |
| 10.7 | 90.7 | 13.2 | 58.3 | 10.6 | 42.6 | 13.8 | 29.0 |
| 10.7 | 65.7 | 13.2 | 55.9 | 10.6 | 35.7 | 12.3 | 29.1 |
| 9.4 | 63.5 | 12.0 | 43.1 | 7.4 | 31.4 | 12.3 | 25.9 |
| 9.4 | 52.9 | 12.0 | 48.6 | 7.4 | 31.4 | 10.4 | 24.3 |
| 6.2 | 53.3 | 10.7 | 44.6 | 6.5 | 29.7 | 10.4 | 24.0 |
| 6.2 | 41.3 | 10.7 | 43.0 | 6.5 | 27.5 | 8.1 | 18.9 |
| 5.0 | 39.0 | 9.6 | 46.2 | 4.5 | 20.1 | 8.1 | 19.4 |
| 5.0 | 45.8 | 9.6 | 48.8 | 4.5 | 22.2 | 7.0 | 21.0 |
| 4.2 | 48.2 | 7.4 | 37.2 | 3.2 | 17.7 | 7.0 | 20.1 |
| 4.2 | 31.7 | 7.4 | 36.8 | 3.2 | 17.9 | 5.2 | 13.7 |
| 4.7 | 29.2 | 5.8 | 29.2 | 3.2 | 18.0 | 5.2 | 12.6 |
| 4.1 | 30.2 | 5.8 | 29.8 | 2.1 | 16.4 | 4.0 | 13.1 |
| 4.1 | 23.5 | 4.5 | 28.6 | 2.1 | 16.8 | 4.0 | 14.9 |
| 3.2 | 24.5 | 4.5 | 26.3 | 11.0 | 34.7 | | |
| 3.2 | 26.0 | 4.1 | 25.6 | 11.0 | 33.1 | | |
| 2.2 | 24.0 | 4.1 | 26.0 | 9.8 | 14.8 | | |
| 2.2 | | 4.1 | 24.8 | 9.8 | 15.7 | | |
| | | 3.3 | 16.5 | 8.4 | 21.3 | | |
| | | 3.3 | 17.6 | 8.4 | 26.9 | | |
| | | | | 8.4 | 22.5 | | |

K(OBS)=  6.79±0.35    K(OBS)=  2.71±C.05    K(OBS)=  2.38±0.01    .K(CES)=  1.52±0.03

K(CO2-HCOOH) = 249±50        (MILLISEC.TORR)$^{-1}$

## TABLE 44

TEMPERATURE (K) = 301.0     CARBONDIOXIDE—FORMIC ACID

(PRESSURE (P) IN TORR AND TAU INVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.014 | | X = 0.010 | | X = 0.005 | |
|---|---|---|---|---|---|
| p | $\tau^{-1}$ | p | $\tau^{-1}$ | p | $\tau^{-1}$ |
| 14.7 | 63.9 | 15.1 | 37.5 | 21.0 | 24.0 |
| 14.7 | 67.0 | 15.1 | 36.0 | 21.0 | 22.3 |
| 12.0 | 66.0 | 13.8 | 40.4 | 19.8 | 26.8 |
| 12.0 | 59.5 | 12.8 | 45.8 | 19.8 | 27.5 |
| 12.0 | 55.4 | 12.8 | 35.3 | 17.9 | 32.7 |
| 10.0 | 50.9 | 12.1 | 38.5 | 17.9 | 33.7 |
| 10.1 | 48.4 | 12.1 | 40.1 | 16.0 | 35.8 |
| 10.1 | 45.2 | 10.4 | 26.9 | 16.0 | 33.4 |
| 8.1 | 46.0 | 10.4 | 28.4 | 14.2 | 19.3 |
| 8.1 | 46.4 | 10.4 | 30.0 | 14.2 | 19.0 |
| 6.5 | 37.7 | 8.8 | 28.0 | 14.2 | 15.7 |
| 5.0 | 39.4 | 8.8 | 37.7 | 13.5 | 20.5 |
| 5.8 | 37.3 | 8.8 | 30.8 | 13.5 | 19.7 |
| 4.7 | 36.3 | 7.2 | 22.0 | 12.2 | 20.6 |
| 4.7 | 31.7 | 7.2 | 24.4 | 12.2 | 24.4 |
| 4.1 | 29.2 | 6.0 | 29.0 | 12.2 | 34.2 |
| 4.1 | 30.2 | 4.0 | 27.2 | 11.0 | 26.9 |
| 4.1 | 23.0 | 4.9 | 20.3 | 11.0 | 26.5 |
| 3.2 | 24.5 | 4.9 | 21.1 | 11.0 | 34.7 |
| 3.0 | 26.0 | 4.1 | 25.6 | 11.0 | 33.1 |
| 2.0 | 24.0 | 4.1 | 26.0 | 9.8 | 14.8 |
|  |  | 4.1 | 24.8 | 9.8 | 15.7 |
|  |  | 3.3 | 16.5 | 8.4 | 21.3 |
|  |  | 3.3 | 17.6 | 8.4 | 26.9 |
|  |  |  |  | 8.4 | 22.5 |

K(OBS) = 3.50±0.00     K(OBS) = 1.88±0.06     K(OBS) = 0.35±0.02

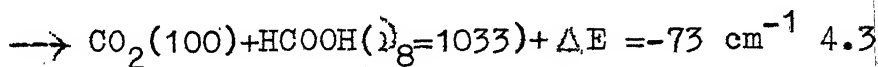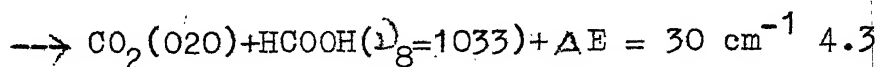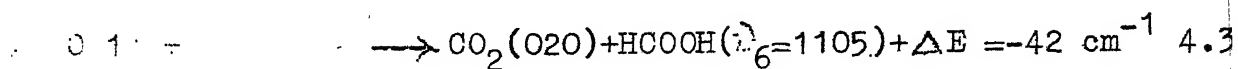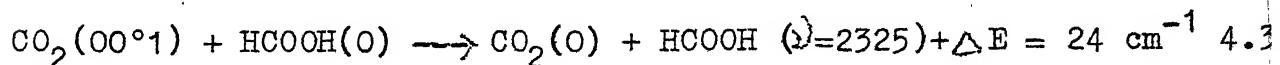K(CO2-HCOOH) = 336±23     (MILLISEC.TORR)$^{-1}$
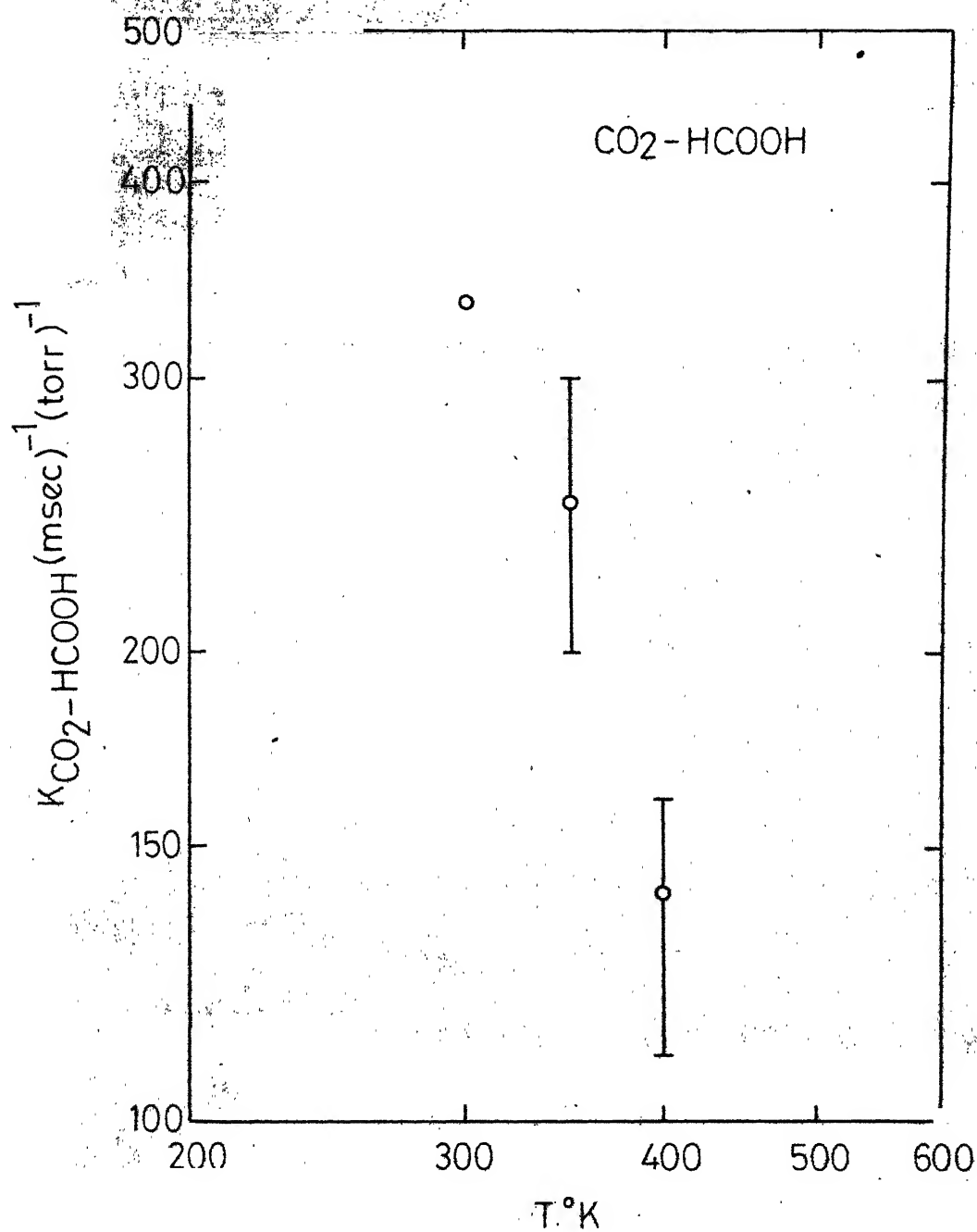
Fig. 12 - Temperature dependence of $K_{CO_2-HCOOH}$

## INTERPRETATION OF RESULTS

In the following we first ignore the dimer formation. The deactivation rate of the $CO_2(00°1)$ mode in collisions with Formic acid (HCOOH) is about two orders of magnitude higher than that with $CO_2$ itself at room temperature and the rates decrease as the temperature increases. This again suggests that near-resonant V-V energy transfer processes could play the dominant role in the deactivation of $CO_2(00°1)$ mode. The fundamental vibrational frequencies of Formic acid are tabulated by Shimonouchi[40]. There is no fundamental band to quench the $CO_2(00°1)$ to the ground state, but there is a weak mixed band at 2325 $cm^{-1(63)}$. The $CO_2(00°1)$ can also be deactivated by a strong fundamental band at 1105 $cm^{-1}(\nu_6)$ identified as the C-O stretch band and a weak band at 1033 $cm^{-1}(\nu_8)$ through the $\nu_3 \longrightarrow 2\nu_2$ and $\nu_3 \longrightarrow \nu_1$ transitions in $CO_2$. Hence the likely processes occuring in the deactivation of $CO_2(00°1)$ level are

$$CO_2(00°1) + HCOOH(0) \longrightarrow CO_2(0) + HCOOH \ (\nu=2325) + \triangle E = 24 \ cm^{-1} \quad 4.3$$

$$0 \ 1 \longrightarrow CO_2(020) + HCOOH(\nu_6=1105) + \triangle E = -42 \ cm^{-1} \quad 4.3$$

$$\longrightarrow CO_2(020) + HCOOH(\nu_8=1033) + \triangle E = 30 \ cm^{-1} \quad 4.3$$

$$\longrightarrow CO_2(100) + HCOOH(\nu_8=1033) + \triangle E = -73 \ cm^{-1} \quad 4.3$$

No attempt has been made to obtain the dipole moments of the transitions of HCOOH involved in the above processes for the following reasons.

1. The experiments could not be carried out beyond 425°K, at which temperature Formic acid starts dissociating.

2. More importantly, even within the temperature range studied, part of the Formic acid exists in dimeric form because of association. The associative nature of this molecule is well studied[64] and it has been observed that the dissociation constant K of the dimers is related to the temperature as

$$\text{Log } K = 10.755 - 3090/T \qquad\qquad 4.40$$

in the temperature range 283-430°K. Here K is in mmHg and T is in °K. Simple calculation from this relation revealed that at room temperature about 64% of the Formic acid is present in the dimeric form and dimer concentration falls to about 1.0% at 400°K at a total pressure of 5 torr. Further, the dimer concentration increases somewhat with increasing pressure. Due to this pressure dependence of the concentration of dimers the determination of $(P\tau_{coll})^{-1}$ from the graph of $\tau^{-1}$ versus P is not reliable.

Evidently the observed decay constant $K_{obs}$ represents the deactivation of $CO_2(00°1)$ mode by monomers as well as dimers and their individual rate contributions could not be separated. In view of this, the value of $K_{CO_2-HCOOH}$ obtained by extrapolation of $K_{obs}$ to 100% of HCOOH cannot be attributed to collisions between $CO_2$ and HCOOH. Thus

the processes 4.36 - 4.39 represents the deactivation of $CO_2(00°1)$ only due to collisions occuring in the mixture with HCOOH monomers. To get a complete picture of the deactivation processes the energy exchange between $CO_2$ and HCOOH dimers must also be included.

## $CO_2-CH_3COOH$
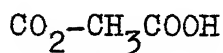
The collisional deactivation of the $CO_2(00°1)$ mode with Acetic acid has been studied at different compositions and several temperatures in the range of 300-750°K. As in the case of the previous systems the fluorescence decay is a single exponential. The complete experimental data has been presented in Tables 43-50 for different temperatures. The deactivation rate constant has been estimated from the fluorescence signals as for the other systems. The temperature dependence of this deactivation rate constant $K_{CO_2-CH_3COOH}$ is presented in Fig.13. The collision cross-sections and the energy transfer probabilities calculated using equations 2.4 and 2.5 at different temperatures are presented in Table 51 along with the deactivation rate constant. As in the case of Formic acid, there is a difficulty in the interpretation of $K_{CO_2-CH_3COOH}$ also, though only at temperatures below 500°K.

# TABLE 48

TEMPERATURE (K) = 750.0    CARBON DIOXIDE-ACETIC ACID

(PRESSURE (P) IN TORR AND TAU INVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.010 | | X = 0.025 | | X = 0.050 | | X = 0.075 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 16.0 | 53.6 | 14.6 | 57.5 | 12.5 | 67.9 | 12.2 | 96.6 |
| 16.0 | 79.4 | 14.6 | 48.6 | 12.5 | 62.8 | 12.2 | 84.7 |
| 14.6 | 70.6 | 13.8 | 46.3 | 11.4 | 69.2 | 11.1 | 79.0 |
| 14.4 | 64.6 | 13.9 | 48.1 | 11.4 | 61.2 | 11.1 | 91.4 |
| 13.2 | 47.4 | 12.2 | 45.7 | 10.2 | 57.2 | 9.8 | 79.7 |
| 13.2 | 48.3 | 12.2 | 48.2 | 10.2 | 52.2 | 9.8 | 77.8 |
| 13.0 | 45.0 | 10.8 | 44.0 | 9.1 | 55.7 | 8.1 | 66.9 |
| 12.1 | 46.7 | 10.8 | 50.1 | 8.9 | 43.4 | 8.1 | 73.7 |
| 12.1 | 52.0 | 9.9 | 49.1 | 8.0 | 59.2 | 6.7 | 68.1 |
| 10.4 | 50.5 | 9.8 | 45.4 | 8.0 | 43.9 | 6.7 | 63.0 |
| 10.6 | 55.5 | 9.2 | 35.1 | 6.9 | 53.9 | 5.6 | 63.3 |
| 9.0 | 45.6 | 8.2 | 41.6 | 6.9 | 54.4 | 5.6 | 49.0 |
| 9.0 | 35.6 | 6.5 | 36.9 | 5.4 | 36.0 | 4.5 | 51.2 |
| 7.4 | 31.6 | 6.9 | 33.2 | 5.4 | 40.0 | 4.5 | 42.2 |
| 7.4 | 22.3 | 5.6 | 31.4 | 4.3 | 33.2 | 3.3 | 42.4 |
| 6.9 | 22.7 | 5.6 | 32.2 | 4.3 | 29.7 | 3.3 | 36.9 |
| 5.9 | 19.9 | 4.0 | 26.3 | 3.2 | 24.1 | 1.9 | 32.2 |
| 4.0 | 24.2 | 4.0 | 27.8 | 3.2 | 26.5 | 1.5 | 27.5 |
| 4.0 | 18.3 | 2.5 | 23.0 | 1.8 | 18.6 | 2.7 | 25.0 |
| 2.4 | 15.8 | 2.5 | 17.9 | 1.8 | 19.5 | 2.7 | 27.2 |
| 2.4 | 15.1 | 4.4 | 26.3 | 2.8 | 35.2 | 2.7 | 29.6 |
| 3.2 | 12.9 | 4.4 | 24.8 | | | | 30.2 |
| | | 3.4 | 23.2 | | | | |
| | | 3.4 | 20.8 | | | | |
| | | 2.0 | 16.3 | | | | |
| | | 2.0 | 17.2 | | | | |

K(OBS)= 4.00±0.06    K(OBS)= 2.49±0.16    K(OBS)= 4.36±0.06    K(OBS)= 6.31±0.11

K(CO2-CH3COOH)= 45.8±26.7    (MILLISEC.TORR)$^{-1}$

## TABLE 64

TEMPERATURE (K)= 700.0          CARBONDIOXIDE-ACETIC ACID
(PRESSURE (P) IN TORR AND TOINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.010 | | X = 0.025 | | X = 0.050 | | X = 0.075 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 15.4 | 73.5 | 20.2 | 91.0 | 21.6 | 94.4 | 12.5 | 85.5 |
| 15.4 | 55.4 | 15.7 | 71.3 | 19.8 | 78.9 | 12.6 | 95.9 |
| 13.0 | 53.4 | 15.7 | 68.3 | 19.8 | 76.8 | 11.1 | 79.1 |
| 13.8 | 50.0 | 13.9 | 72.7 | 15.4 | 63.8 | 11.1 | 66.1 |
| 12.7 | 33.2 | 13.9 | 71.2 | 15.4 | 72.2 | 11.1 | 68.2 |
| 12.7 | 42.0 | 12.4 | 63.2 | 13.8 | 73.0 | 10.1 | 66.3 |
| 12.7 | 41.1 | 12.4 | 72.7 | 13.8 | 65.3 | 10.1 | 84.2 |
| 11.6 | 44.3 | 10.3 | 39.6 | 11.8 | 61.3 | 8.9 | 58.3 |
| 11.4 | 43.7 | 10.3 | 52.9 | 11.8 | 50.7 | 8.9 | 43.6 |
| 10.7 | 38.7 | 10.1 | 79.7 | 10.0 | 42.8 | 8.6 | 47.9 |
| 10.7 | 34.0 | 8.5 | 37.8 | 10.0 | 55.0 | 8.6 | 43.1 |
| 9.0 | 33.5 | 8.5 | 39.0 | 7.6 | 43.0 | 6.5 | 31.5 |
| 9.0 | 30.3 | 6.5 | 33.0 | 7.6 | 40.6 | 6.5 | 45.3 |
| 7.0 | 27.5 | 6.5 | 33.9 | 6.2 | 41.2 | 5.6 | 34.0 |
| 7.7 | 28.4 | 4.8 | 24.2 | 6.2 | 37.9 | 5.6 | 38.1 |
| 6.7 | 29.8 | 4.8 | 24.3 | 4.2 | 33.1 | 4.6 | 36.2 |
| 6.7 | 33.3 | 3.2 | 20.2 | 4.2 | 27.9 | 4.6 | 38.3 |
| 5.0 | 20.0 | 3.2 | 21.3 | 3.8 | 44.6 | 3.8 | 34.0 |
| 5.0 | 17.0 | 1.7 | 16.2 | 3.8 | 44.2 | 3.8 | 28.0 |
| 3.2 | 13.7 | 1.7 | 15.2 | 2.9 | 29.4 | 2.7 | 27.2 |
| 3.2 | 22.0 | 4.4 | 26.3 | 2.8 | 35.2 | 2.7 | 29.6 |
| 3.2 | 12.8 | 4.4 | 24.8 | | | 2.7 | 30.2 |
| | | 3.4 | 23.2 | | | | |
| | | 3.4 | 20.8 | | | | |
| | | 2.0 | 16.3 | | | | |
| | | 2.0 | 17.1 | | | | |

K(OBS)= 3.38±0.03     K(OBS)= 4.43±0.02     K(OBS)= 3.31±0.08     K(OBS)= 5.86±0.20

K(CO2-CH3COOH)= 39.7±23.9 (MILLISEC.TORR)$^{-1}$

# TABLE 46

TEMPERATURE (K)= 650.0  CARBONDIOXIDE-ACETICACID

(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.010 | | X = 0.025 | | X = 0.050 | | X = 0.075 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 16.0 | 54.5 | 12.5 | 54.1 | 11.7 | 91.4 | 11.4 | 94.4 |
| 16.0 | 45.7 | 12.5 | 59.0 | 10.7 | 71.8 | 10.3 | 88.1 |
| 14.2 | 49.4 | 11.3 | 47.0 | 9.8 | 79.3 | 10.3 | 93.7 |
| 14.5 | 48.7 | 11.3 | 60.8 | 8.3 | 70.8 | 9.5 | 98.7 |
| 12.4 | 45.0 | 10.0 | 46.2 | 8.8 | 71.8 | 9.5 | 82.9 |
| 12.4 | 38.2 | 10.0 | 45.2 | 7.7 | 60.0 | 8.6 | 93.7 |
| 11.1 | 41.9 | 8.7 | 46.2 | 7.7 | 57.9 | 8.5 | 83.0 |
| 11.1 | 41.2 | 8.7 | 42.7 | 6.2 | 45.2 | 7.9 | 89.1 |
| 9.6 | 35.9 | 7.6 | 35.5 | 6.2 | 47.0 | 7.9 | 79.8 |
| 9.6 | 32.6 | 5.3 | 38.7 | 5.1 | 35.6 | 6.1 | 74.8 |
| 7.0 | 24.3 | 6.3 | 35.4 | 5.1 | 43.8 | 6.1 | 62.8 |
| 7.0 | 21.0 | 5.2 | 34.1 | 4.0 | 33.3 | 4.6 | 58.7 |
| 6.0 | 22.7 | 5.2 | 34.9 | 4.0 | 36.5 | 4.6 | 54.2 |
| 6.3 | 22.0 | 4.0 | 22.3 | 2.8 | 23.2 | 3.6 | 44.1 |
| 4.0 | 15.7 | 4.0 | 22.6 | 2.8 | 21.5 | 3.5 | 47.3 |
| 4.0 | 20.3 | 2.8 | 17.5 | 1.9 | 23.7 | 2.3 | 33.2 |
| 3.0 | 15.8 | 2.8 | 18.8 | 1.9 | 20.8 | 2.3 | 33.2 |
| 3.0 | 14.0 | 2.8 | 18.1 | 3.8 | 44.6 | 1.8 | 27.6 |
| 2.0 | 12.9 | 1.7 | 16.2 | 3.8 | 44.2 | 3.1 | 44.0 |
| 2.0 | 11.8 | 1.7 | 15.2 | 2.8 | 28.4 | 2.2 | 32.2 |
|  |  | 4.4 | 26.3 | 2.8 | 35.2 | 2.2 | 36.7 |
|  |  | 4.4 | 24.8 |  |  |  |  |
|  |  | 3.4 | 23.7 |  |  |  |  |
|  |  | 3.4 | 20.8 |  |  |  |  |
|  |  | 2.0 | 15.3 |  |  |  |  |
|  |  | 2.0 | 17.1 |  |  |  |  |

K(OBS)= 2.95±0.02   K'OBS)= 3.88±0.02   K(OBS)= 7.04±0.07   K(OBS)= 7.22±0.21

K(CO2-CH3COOH)= 78.9±20.   (MILLISEC.TORR)$^{-1}$

## TABLE 46

CARBONDIOXIDE-ACETICACID

TEMPERATURE (K) = 600.0

(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.010 | | X = 0.025 | | X = 0.050 | | X = 0.075 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 22.0 | 62.9 | 12.9 | 58.7 | 9.9 | 100.4 | 8.3 | 86.3 |
| 19.0 | 55.3 | 12.9 | 63.5 | 9.9 | 99.1 | 8.3 | 93.6 |
| 19.0 | 53.5 | 11.9 | 59.0 | 9.3 | 87.7 | 7.5 | 92.1 |
| 15.0 | 40.0 | 11.9 | 60.0 | 8.2 | 82.4 | 7.6 | 82.1 |
| 13.0 | 42.3 | 11.5 | 54.0 | 8.2 | 86.0 | 6.3 | 79.3 |
| 13.0 | 36.5 | 11.5 | 59.2 | 7.6 | 68.7 | 6.8 | 81.0 |
| 12.0 | 35.4 | 11.5 | 59.3 | 5.6 | 57.2 | 6.1 | 72.3 |
| 12.0 | 31.0 | 10.5 | 59.8 | 5.6 | 53.4 | 5.1 | 69.0 |
| 10.0 | 30.6 | 10.5 | 53.0 | 4.7 | 54.0 | 5.1 | 73.9 |
| 10.0 | 30.7 | 9.6 | 47.8 | 4.7 | 51.9 | 5.1 | 63.7 |
| 9.0 | 28.2 | 9.6 | 45.0 | 3.9 | 41.7 | 4.5 | 58.5 |
| 8.0 | 23.5 | 9.0 | 44.6 | 3.9 | 39.8 | 4.5 | 56.6 |
| 6.0 | 22.7 | 9.0 | 45.4 | 2.9 | 36.0 | 3.7 | 54.3 |
| 6.2 | 16.9 | 8.0 | 43.8 | 2.9 | 33.9 | 3.7 | 45.5 |
| 4.0 | 16.7 | 8.0 | 41.4 | 1.8 | 22.1 | 2.9 | 35.0 |
| 4.0 | 13.2 | 8.0 | 41.4 | 1.8 | 22.4 | 2.9 | 39.1 |
| 2.5 | 9.9 | 6.8 | 43.9 | 4.6 | 42.6 | 1.5 | 35.6 |
| 2.5 | 18.0 | 6.8 | 34.9 | 3.8 | 44.6 | 1.8 | 27.6 |
| 2.5 | 18.9 | 5.5 | 32.1 | 3.8 | 44.2 | 3.1 | 44.0 |
| 2.4 | | 5.5 | 27.0 | 2.8 | 28.4 | 2.2 | 32.2 |
| | | 4.4 | 26.3 | 2.8 | 35.2 | 2.2 | 36.7 |
| | | 4.4 | 24.8 | | | | |
| | | 3.4 | 23.2 | | | | |
| | | 3.4 | 20.8 | | | | |
| | | 2.0 | 16.3 | | | | |
| | | 2.0 | 17.1 | | | | |

K(OBS) = 2.47±0.02  K(OBS) = 4.30±0.02  K(OBS) = 8.85±0.07  K(OBS) = 9.48±0.22

K(CO2-CH3COOH) = 118±26  (MILLISEC.TORR)$^{-1}$

TABLE 49

TEMPERATURE (K) = 550.0       CARBONDIOXIDE-ACETICACID
(PRESSURE (P) IN TORR   AND   TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.010 | | X = 0.025 | | X = 0.050 | | X = 0.075 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 12.0 | 41.2 | 10.9 | 36.0 | 11.5 | 96.1 | 10.0 | 95.3 |
| 12.5 | 49.7 | 9.5 | 27.9 | 11.5 | 102.9 | 10.0 | 128.1 |
| 11.1 | 41.9 | 9.5 | 27.0 | 10.4 | 55.2 | 8.7 | 86.5 |
| 11.1 | 41.2 | 8.1 | 23.0 | 10.4 | 67.1 | 8.7 | 82.2 |
| 10.7 | 40.4 | 8.1 | 27.1 | 10.4 | 65.5 | 8.2 | 113.0 |
| 10.2 | 37.8 | 7.0 | 22.0 | 9.4 | 58.8 | 8.2 | 106.3 |
| 8.9 | 32.1 | 7.0 | 22.3 | 9.4 | 49.1 | 7.0 | 103.3 |
| 7.6 | 27.1 | 6.1 | 18.4 | 8.5 | 67.9 | 7.0 | 102.6 |
| 7.6 | 24.7 | 6.1 | 17.4 | 9.5 | 63.3 | 6.3 | 94.5 |
| 5.9 | 21.8 | 5.0 | 20.4 | 7.4 | 61.6 | 6.3 | 85.6 |
| 5.3 | 19.8 | 5.0 | 20.8 | 7.4 | 63.3 | 5.5 | 66.0 |
| 5.3 | 19.8 | 3.8 | 18.7 | 6.5 | 52.9 | 5.6 | 81.2 |
| 4.1 | 16.1 | 3.8 | 16.7 | 6.5 | 50.8 | 5.5 | 79.2 |
| 4.1 | 17.1 | 3.1 | 17.2 | 5.4 | 50.5 | 4.8 | 69.6 |
| 3.2 | 19.2 | 3.1 | 18.3 | 5.4 | 53.9 | 4.8 | 71.5 |
| 3.2 | 19.1 | 2.2 | 10.7 | 4.6 | 40.0 | 4.1 | 50.8 |
| 3.5 | 13.2 | 2.2 | 13.4 | 4.6 | 42.6 | 4.1 | 56.3 |
| 2.5 | 8.9 | 2.4 | 18.6 | 3.8 | 44.6 | 3.1 | 40.2 |
| 2.6 | 18.0 | | | 3.8 | 44.2 | 3.1 | 44.0 |
| 2.5 | 18.9 | | | 2.8 | 28.4 | 2.2 | 32.2 |
| | | | | 2.8 | 35.2 | 2.2 | 36.7 |

K(OBS)= 3.29±0.07    K(OBS)= 2.07±0.01    K(OBS)= 5.22±0.03    K(OBS)= 10.07±0.12

K(CO2-CH3COOH)= 109±36      (MILLISEC.TORR)$^{-1}$

## TABLE 48

### CARBONDIOXIDE-ACETIC ACID

TEMPERATURE (K)= 500.0

(PRESSURE (P) IN TORR AND TO INVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| Y = 0.010 | | X = 0.025 | | X = 0.050 | | X = 0.075 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 15.0 | 40.7 | 12.7 | 63.2 | 7.9 | 73.4 | 7.8 | 112.4 |
| 15.0 | 44.8 | 12.7 | 62.0 | 7.9 | 64.4 | 7.8 | 113.3 |
| 13.5 | 34.8 | 11.2 | 50.6 | 7.9 | 68.9 | 7.2 | 112.0 |
| 13.5 | 36.7 | 11.2 | 39.7 | 7.0 | 57.5 | 7.2 | 97.2 |
| 12.0 | 35.5 | 9.9 | 36.1 | 7.0 | 54.6 | 6.7 | 102.5 |
| 12.0 | 33.4 | 9.9 | 33.5 | 6.1 | 56.7 | 6.7 | 113.6 |
| 10.0 | 27.1 | 8.6 | 29.8 | 5.4 | 47.3 | 6.2 | 99.9 |
| 9.1 | 23.4 | 8.6 | 41.9 | 5.4 | 55.1 | 6.2 | 99.3 |
| 9.1 | 29.2 | 6.4 | 29.2 | 4.8 | 40.2 | 5.4 | 78.6 |
| 8.3 | 24.9 | 6.4 | 33.6 | 4.8 | 50.8 | 5.4 | 86.8 |
| 8.3 | 24.3 | 5.1 | 25.6 | 4.5 | 47.3 | 5.0 | 73.4 |
| 8.3 | 22.8 | 5.1 | 25.5 | 4.5 | 39.2 | 5.0 | 80.8 |
| 7.5 | 16.7 | 4.0 | 21.9 | 4.0 | 43.3 | 4.0 | 71.4 |
| 7.5 | 21.4 | 4.0 | 29.2 | 4.0 | 43.7 | 4.0 | 66.7 |
| 5.4 | 19.0 | 3.2 | 26.5 | 3.0 | 39.4 | 3.3 | 52.0 |
| 3.0 | 18.3 | 3.2 | 22.6 | 3.0 | 33.4 | 3.3 | 58.3 |
| 3.0 | 20.4 | 2.4 | 14.1 | 2.2 | 24.7 | 2.4 | 41.7 |
| 2.6 | 18.0 | 2.4 | 18.6 | 2.2 | 24.6 | 2.4 | 43.7 |
| 2.5 | 18.9 | | | 1.6 | 30.1 | 1.5 | 34.3 |
| | | | | 1.6 | 26.5 | 1.6 | 31.1 |

K(OBS)= 2.51±0.05     K(OBS)= 3.44±0.03     K(OBS)= 6.52±0.04     K(OBS)= 13.38±0.12

K(CO2-CH3COOH)= 156 ± 33   (MILLISEC.TORR)$^{-1}$

## TABLE 49

TEMPERATURE (K) = 400.0    CARBONDIOXIDE-ACETICACID

(PRESSURE (P) IN TORR AND TOWINVERSE ($\tau^{-1}$) IN INVERSE MILLISEC.)

| X = 0.010 | | X = 0.025 | | X = 0.050 | | X = 0.075 | |
|---|---|---|---|---|---|---|---|
| P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ | P | $\tau^{-1}$ |
| 16.0 | 40.4 | 12.3 | 90.0 | 9.1 | 195.3 | 6.4 | 118.4 |
| 16.0 | 35.6 | 12.3 | 92.3 | 9.1 | 173.3 | 6.4 | 113.5 |
| 14.0 | 32.6 | 11.1 | 81.2 | 8.2 | 147.7 | 3.7 | 75.7 |
| 14.0 | 32.5 | 11.1 | 87.8 | 8.2 | 151.1 | 3.7 | 69.8 |
| 13.0 | 33.3 | 8.1 | 59.9 | 7.9 | 119.6 | 2.4 | 52.7 |
| 12.2 | 32.5 | 8.1 | 67.4 | 4.9 | 75.9 | 2.4 | 56.2 |
| 12.0 | 34.3 | 7.3 | 55.8 | 4.9 | 78.6 | 1.6 | 40.3 |
| 10.2 | 30.0 | 7.3 | 66.7 | 3.6 | 78.1 | 1.6 | 36.2 |
| 10.2 | 31.5 | 4.8 | 42.9 | 3.8 | 83.2 | | |
| 8.0 | 28.5 | 4.8 | 46.7 | 3.0 | 54.0 | | |
| 8.2 | 23.0 | 3.2 | 41.6 | 3.0 | 54.4 | | |
| 6.5 | 23.8 | 3.2 | 36.4 | 2.0 | 45.8 | | |
| 6.4 | 22.0 | 2.1 | 27.2 | 1.2 | 46.5 | | |
| 5.4 | 22.6 | 2.1 | 30.2 | 1.2 | 39.1 | | |
| 5.0 | 19.0 | | | | | | |
| 3.0 | 18.3 | | | | | | |
| 3.0 | 20.4 | | | | | | |
| 2.5 | 18.0 | | | | | | |
| 2.5 | 18.9 | | | | | | |

K(OBS) = 1.50±0.04    K(OBS) = 5.98±0.02    K(OBS) = 17.06±0.42    K(OBS) = 15.92±0.49

K(CO2-CH3COOH) = 239 ± 81    (MILLISEC.TORR)$^{-1}$

## TABLE 39

TEMPERATURE (K)= 301.0

(PRESSURE (P) IN TORR AND $\tau^{-1}$ IN INVERSE MILLISEC.)

CARBONDIOXIDE-ACETICACID

| X = C.Cl₃ | | | X = 0.025 | |
|---|---|---|---|---|
| p | $\tau^{-1}$ | | p | $\tau^{-1}$ |
| 3.7 | 20.6 | | 10.5 | 124.0 |
| 3.7 | 17.9 | | 10.5 | 164.0 |
| 2.8 | 19.4 | | 9.6 | 130.9 |
| 2.8 | 16.7 | | 9.6 | 149.6 |
| | | | 8.7 | 142.5 |
| | | | 8.7 | 123.5 |
| | | | 7.9 | 118.8 |
| | | | 7.9 | 114.7 |
| | | | 7.2 | 105.3 |
| | | | 7.2 | 102.4 |
| | | | 6.2 | 115.9 |

K(OBS)= 1.36±0.33

K(OBS)= 10.09±1.74

K(CO2-CH3CCOH) = 405±152    (MILLISEC.TORR)$^{-1}$
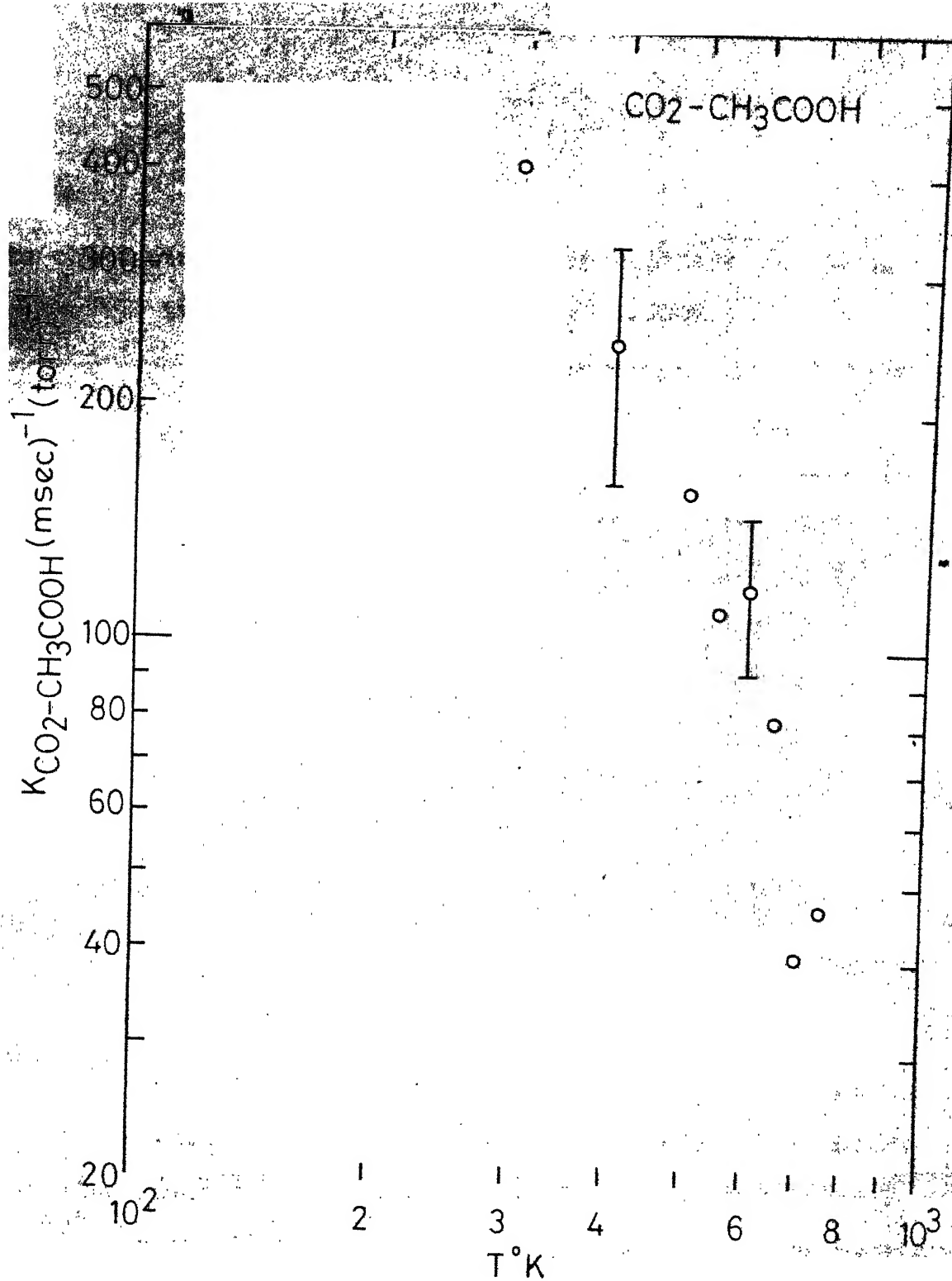
Fig. 13 - Temperature dependence of $K_{CO_2-CH_3COOH}$

Table 51

Rate constants, cross-sections and probabilities of energy

transfer from $CO_2(00°1)$ to $CH_3COOH$

| $T°K$ | $K_{CO_2-M}(ms^{-1}torr^{-1})$ | $\sigma-\overset{\circ}{A}^2$ | $P_{exp}x10^2$ |
|---|---|---|---|
| 301 | 405 ± 152 | 2.47 ± 0.93 | 4.18 ± 1.57 |
| 400 | 239 ± 81 | 1.68 ± 0.57 | 2.85 ± 0.96 |
| 500 | 156 ± 33 | 1.23 ± 0.26 | 2.08 ± 0.44 |
| 550 | 109 ± 36 | 0.89 ± 0.3 | 1.52 ± 0.5 |
| 600 | 118 ± 26 | 1.02 ± 0.22 | 1.72 ± 0.37 |
| 650 | 78.9± 20.0 | 0.70 ± 0.18 | 1.2 ± 0.3 |
| 700 | 39.7± 23.9 | 0.37 ± 0.22 | 0.62 ± 0.38 |
| 750 | 45.8± 26.7 | 0.44 ± 0.23 | 0.74 ± 0.04 |

INTERPRETATION OF RESULTS

Again we first ignore dimer formation in this molecule
also. The magnitude and the temperature dependence of the de-
activation rates for this system are similar to those for Formic
acid. So, as in the case of Formic acid, near-resonant processes
must be dominant in the deactivation of the $CO_2$ asymmetric mode
by Acetic acid molecules. The vibrational frequencies of the
fundamental bands of Acetic acid are reported by Shimanouchi[40]

and those of the mixed and overtone bands by Wilmshurt[65]. Based
on these frequencies, the following processes may be expected
to cause the deactivation of the $CO_2(00°1)$ mode.

$$CO_2(00°1) + CH_3COOH \ (0) \longrightarrow CO_2(0)+CH_3COOH(\nu=2212)+\Delta E =137 \ cm^{-1} \quad 4.41$$

$$\longrightarrow CO_2(0)+CH_3COOH(\nu=2513)+\Delta E =-164 cm^{-1} \quad 4.42$$

$$\longrightarrow CO_2(0)+CH_3COOH(\nu=2283)+\Delta E = 66 \ cm^{-1} \quad 4.43$$

$$\longrightarrow CO_2(100)+CH_3COOH(\nu_9=989)+\Delta E=-29 \ cm^{-1} \quad 4.44$$

$$\longrightarrow CO_2(100)+CH_3COOH(\nu_{10}=847)+\Delta E=113 cm^{-1} \quad 4.45$$

$$\longrightarrow CO_2(020)+CH_3COOH(\nu_8=1182)+\Delta E=-119 cm^{-1} \quad 4.46$$

$$\longrightarrow CO_2(020)+CH_3COOH(\nu_{15}=1048)+\Delta E=15 \ cm^{-1} \quad 4.47$$

$$\longrightarrow CO_2(020)+CH_3COOH(\nu_9=989)+\Delta E=74 \ cm^{-1} \quad 4.48$$
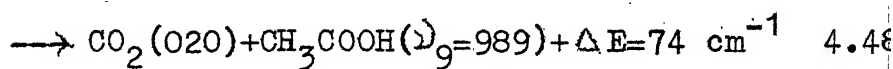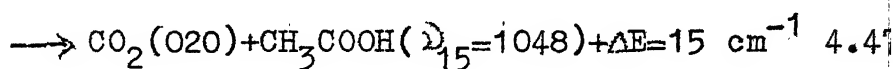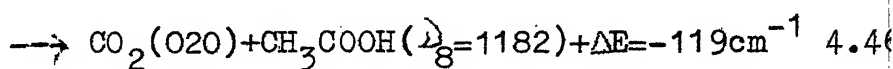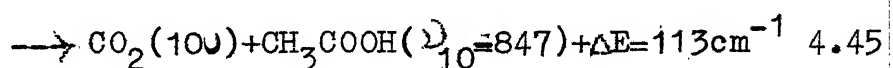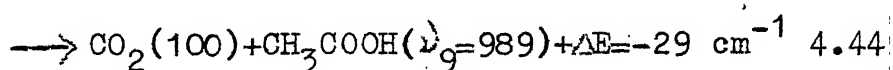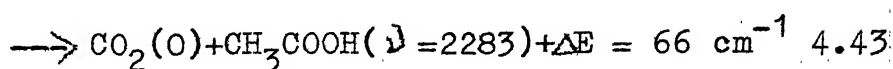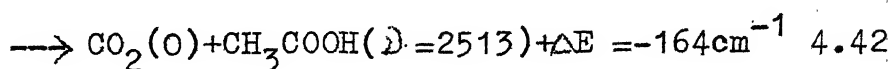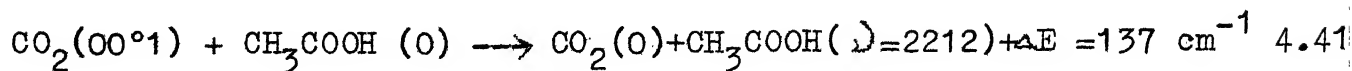
All the three mixed mode transitions of Acetic acid in
processes 4.41 and 4.42 and 4.43 are weak. Even though 4.41 and
4.42 involve a large energy mismatch, they can not be dropped
because the $\nu_3 \longrightarrow 0$ transition of $CO_2$ is very strong and their
contribution might be comparable to that of 4.43. The $\nu_9 \longrightarrow 0$
transition in 4.44 and 4.45 is of medium strength. Even
though the $CO_2$ transitions involved in these are less intense,
these processes could not be dropped because the energy mis-
matches are not large. The transition $\nu_{10} \longrightarrow 0$ in process 4.45

is weak with a large energy mismatch and a less intense $CO_2$ transition. Hence this process can be neglected. Process 4.46 involving larger energy mismatch cannot be dropped since the $\nu_8 \longrightarrow 0$ (C-O stretch) transition is strong. The transition $\nu_{15} \longrightarrow 0$ in process 4.47 is weak but can not be dropped because this involves a small energy mismatch. Hence except process 4.45, all the others are likely to contribute to the total deactivation.

No attempt has been made to estimate the transition moments for this system also because of the following reasons.

1. A large number of processes are involved in the deactivation of $CO_2(00°1)$.

2. Acetic acid, like Formic acid, is highly associative at room temperature and the dissociation constant of dimers is given by[66,67]

$$Log \ K = 11.789 - 3590/T \qquad \qquad 4.49$$

in the temperature range of 298-728°K,

where K is the dimer dissociation constant in mmHg and T is the temperature in °K.

At room temperature and a pressure of 5 torr about 82% of this acid exists as dimers and this concentration falls to 1.5% at 400°K and is negligible at 500°K and the

concentration of dimers increases as the pressure is increased. Hence, part of the measured deactivation rate is due to dimers at 300 and 400°K. Therefore, all the comments made regarding the interpretation of $K_{obs}$ and $K_{CO_2-M}$ in the case of M=HCOOH are also applicable to Acetic acid at temperatures where the dimer concentration is appreciable.

Thus the temperature range that can be used for estimating the transition moments is narrowed down to 500-750°K. It is felt that this temperature range is too small to estimate the transition moments in view of the large number of processes involved.

# CHAPTER V

## CONCLUSIONS

The Laser Induced Fluorescence technique has been used to measure the deactivation rates of the asymmetric stretch mode of $CO_2$ in collisions with polyatomic molecules. The polyatomic molecules studied are $CH_3OH$, $CH_3OD$, $C_2H_5OH$, $C_2H_4O$, $CH_3CHO$, $HCOOH$ and $CH_3COOH$. These measurements have been carried out at those temperatures where no dissociation of these molecules occured in the range of 300-750°K. The studies have been limited to lean mixtures of the polyatomic molecules, all below 12.5%, due to the limitations imposed by the time constant of the detector and the associated electronic circuitry, which is $< 2\,\mu$ sec. The lean mixture data is extrapolated to 100% of polyatomic gas composition to get the deactivation rate $K_{CO_2-M}$ of $CO_2$ with the poly-atomic molecule M. The measured deactivation rates are in the range of 20-400 $msec^{-1}torr^{-1}$ and decreased with increasing temperature.

The deactivation rates of the CO(v=1) mode with the above polyatomic molecules (with the exception of $CH_3OD$ and $C_2H_4O$) are measured[68] at room temperature and are 5.9, 5.9, 4.7, 11.7 and 20 $msec^{-1}torr^{-1}$ for $CH_3OH$, $C_2H_5OH$, $CH_3CHO$, HCOOH and $CH_3COOH$ respectively. These rates are quite small since only the bands around 2150 $cm^{-1}$, which are all weak,

can cause deactivation of CO $(v=1)$. The corresponding rates of deactivation of $CO_2(00°1)$ mode obtained in the present work are about 17, 35, 10, 28 and 20 times faster than those for the CO$(v=1)$ deactivation by the same molecules respectively. These enhanced rates are due to the additional deactivation channels available in $CO_2$ for the transfer of energy through $(00°1 \longrightarrow 020, 100)$ transitions and the existence of very strong/strong fundamental vibrational bands in the polyatomic molecules to take the energy by near-resonant V-V processes. In the alcohols it is the very strong C-O stretch which is responsible for the enhanced rate while in $C_2H_4O$ two very strong ring deform vibrations are responsible and in $CH_3CHO$ the strong C-C stretch and the medium $CH_3$ rock bands are responsible. Since only strong and medium bands are responsible for the deactivation in the case of $CH_3CHO$, it is the least efficient of the seven polyatomic molecules studied.

In the case of the two acids, the deactivation rates are even larger. However, because of dimer formation in the vapor phase, the reliability of $K_{CO_2-HCOOH}$ and $K_{CO_2-CH_3COOH}$ obtained by extrapolation to zero percent of $CO_2$ is uncertain.

The dipole moments of the transitions involved in the polyatomic molecules are estimated. This is done with the

help of the experimentally derived probabilities at diffe-
rent temperatures and the SB theory. These estimated tran-
sition moments are approximate to the extent that the SB
theory is approximate. However, these moments are in agree-
ment with the relative intensities of the transitions as
reported from spectroscopic measurements[40]. If these tra-
nsition moments can be measured independently, these cal-
culations can be used to test the validity of the SB theory
for such calculations in polyatomic molecules.

The useful temperature range for the above calcu-
lations in the case of the Carboxylic acids is reduced due
to association at the lower temperatures. Considering the
fact that the number of processes involved in these mole-
cules is relatively large with respect to the available
temperature range, no attempt has been made to calculate
the transition moments.

## REFERENCES

1. C.K.N. Patel, Phys.Rev. Letts., 12, 588 (1964) and
   13, 617 (1964)

2. C.K.N. Patel, W.L.Faust and R.A. McFarlane, Bull. Amer.
   Phys. Soc., 9, 500 (1964)

3. C.K.N. Patel, P.K.Tien and J.H. McFee, Appl. Phys. Letts,
   7, 290 (1965)

4. G.Moeller and J.D. Rigden, Appl. Phys.Letts, 7, 274 (1965)

5. O.P. Judd, Appl. Phys. Letts, 22, 95 (1973)

6. E.T. Gerry, IEEE Spectrum, 7(11), 51 (1970)

7. C.K.N. Patel in "Lasers" Vol.2, ed. Levine, chapter 1,
   Marcel Dekker, New York (1968)

8. N.V. Karlov, Appl. Optics, 13, 310 (1974)

9. J.C. Stephenson and S.M. Freud, J.Chem.Phys., 65, 1893 (1976)

10. J.M.Press, R.E. Weston Jr and G.W. Flynn, Chem.Phys.Letts
    46, 69 (1977)

11. C.B. Moore in "Fluorescence" ed. by Gilbault, chapter 3,
    Marcel Dekker, New York (1967)

12. R.D. Sharma and C.A. Brau, J.Chem.Phys., 50, 924 (1969)

13. R.N. Schwartz, Z.I. Slawsky and Herzfeld, J.Chem. Phys., 20,
    1591 (1952)

14. F.I. Tanczos, J.Chem.Phys., 25, 439 (1956)

15. F.H. Mies, J.Chem.Phys., 42, 2709 (1965)

16. J.L. Stretton in "Transfer and storage of energy by mole-
    cules" ed. by G.M. Burnett and A.M. North, chapter 2,
    John Wiley (1969)

17. K.F. Herzfeld and T.F. Litovitz in "Absorption and disper-
    sion of Ultrasonic waves", Academic Press, London (1959)

18. C.B. Moore in "Advances in Chem.Phys.", ed. by I.Prigogine and S.A. Rice, Vol.23, chapter 2, John Wiley (1972)

19. J.D. Stettler and N.M. Witriol, Chem.Phys.Letts, 23, 95 (1973)

20. P.D. Gait, Chem.Phys.Letts. 41, 236 (1976)

21. J.D. Stettler and N.M. Witriol, Chem.Phys.Letts. 41,241(1976)

22. W.G. Tam, Chem.Phys.Letts. 15, 113 (1972)

23. R.D. Sharma, Chem.Phys. Letts. 30, 261 (1975)

24. T.A. Dillon and J.C. Stephenson J.Chem.Phys. 58, 2056,3849 (1973) and 60, 4286 (1974)

25. R.C. Amme in "Advances in Chem.Phys.", ed. by I.Prigogine and S.A. Rice, Vol.28, Chapter 3, John Wiley (1975)

26. Stephen Ormonde, Rev. Modern Phys. 47, 193 (1975)

27. L.O. Hocker, M.A. Kovacs, C.K. Rhodes, G.W. Flynn and A. Javan, Phys.Rev.Letts. 17, 233 (1966)

28. J.T. Yardley and C.B. Moore, J.Chem.Phys. 45, 1066 (1966)

29. G.W. Flynn in "Chemical and biological applications of lasers" ed. by C.B. Moore, chapter 6, Academic Press (1974)

30. E.Weitz and G.W. Flynn in"Annual Rev.Phys.Chem.", ed. by H.Eyring, Vol.25,Annual review incorp. Co.(1974)

31. A.J. Andrews and C.J. S.M. Simpson, Chem.Phys. Letts 41, 565 (1976)

32. R.J. Pirkle and T.A.Cool, Chem.Phys.Letts, 42, 58 (1976)

33. L.A. Gamss, B.H. Kohn, M.I. Pollack and A.M. Ronn, Chem. Phys. 18, 85 (1976)

34. M.A.Kovacs, D.R. Rao and A.Javan, J.Chem.Phys. 48, 3339(1968)

35. Y.V.Chalapati Rao, V.Subba Rao and D. Ramachandra Rao, Chem.Phys.Letts. 17, 531 (1972) and Y.V. Chalapati Rao, Ph.D. Thesis, I.I.T.Kanpur, 1972

36. P. Ramamohana Rao, Y.V.Chalapati Rao, S.V.Babu and V.Subba Rao, Ind. J.Phys. 50, 259 (1976) and Proceedings of the "DAE Chemistry Symposium on Fast reactions, chemistry and measurement" held at VSSC, Trivandrum, February 17-21, 1977, to be published.

37. I.V.Rao, Ph.D. Thesis, I.I.T. Kanpur (1976)

38. W.A. Rosser Jr, A.D. Wood and E.T. Gerry, J.Chem.Phys., 50, 4996 (1969)

39. C.B. Moore, Acc. Chem. Research 2, 103 (1969)

40. T. Shimanouchi, Tables of molecular vibrational frequencies, consolidated Volume I, NSRDS-NBS 39 (National Bureau of Standards, Washington, 1971)

41. M.Filk and E. Whalley, J.Chem.Phys. 34, 1554 (1964)

42. L.Landau and E.Teller, Z.Phys. Sowjetunion, 10, 34 (1936)

43. I. Burak, Y.Noter, A.M. Ronn and A.Szoke, Chem.Phys.Letts, 16, 306 (1972)

44. R.D. Sharma, H.L. Chen and A. Szoke, J.Chem.Phys., 58, 3519 (1973)

45. W.Q. Jeffers and J.D. Kelly, J.Chem.Phys. 55, 4433 (1971)

46. R.D. Sharma, Phys.Rev., 177, 102 (1969)

47. B.M. Hopkins, H.L. Chen and R.D. Sharma, J.Chem.Phys. 59, 5758 (1973)

48. W.A. Rosser Jr, R.D. Sharma and E.T. Gerry, J.Chem.Phys. 54, 1196 (1971)

49. D.Frankel, J.I. Steinfeld, R.D. Sharma and L. Poulsen, Chem.Phys.Letts. 28, 485 (1974)

50. R.D. Sharma and C.W. Kern, J.Chem.Phys., 55, 1171 (1971)

51. I.W.M. Smith and C. Morley, Trans. Farad Soc., 67, 2575 (1971)

52. R.D. Sharma, R.B.Malk, R.R.Hart and R.H. Picard, Chem. Phys.Letts. 35, 286 (1975)

53. J.O. Hirschfelder, C.F.Curtiss and R.B. Bird, <u>Molecular Theory of Gases and Liquids</u> (Wiley,New York, 1954)

54. P.Venkateswarlu and W. Gordy, J.Chem.Phys.,<u>23</u>, 1200 (1955)

55. E.K. Plyler, J.Research NBS, <u>48</u>, 281 (1952)

56. L.M.Imanov, Ch.O.Kadzhar and I.D.Isaev, Optics and spectroscopy <u>18</u>, 194 (1965)

57. R.C.Lord and N.B.Nolin, J.Chem.Phys., <u>24</u>, 656 (1956)

58. H.W.Thompson and W.T.Cave, Trans.Farad Soc. <u>47</u>, 946 (1951)

59. JANAF Thermochemical Tables (U.S.Dept. of Commerce,NBS,1965)

60. S.M. Sverdlov, M.A.Kovner and E.P.Krainov, <u>Vibrational spectra of polyatomic molecules</u>, John Wiley (1974)

61. J.C. Evans and H.T. Bernstein, Can.J. Chem. <u>34</u>, 1084 (1956)

62. J.C. Morris, J.Chem.Phys.,<u>11</u>, 230 (1943)

63. L.G.Boner and R.Hofstadter, J.Chem.Phys. <u>6</u>, 531 (1938)

64. A.S. Coolidge, J.Amer.Chem.Soc. <u>50</u>, 2166 (1928)

65. J.K.Wilmshurst, J.Chem. Phys., <u>25</u>, 1171 (1956)

66. F.M.Mac Daugall, J.Amer.Chem.Soc. <u>58</u>, 2585 (1936)

67. R.M. Badger and S.H.Bauer, J.Chem.Phys.,<u>5</u>, 605 (1937)

68. J.C.Stephenson and E.R. Mosburg, J.Chem.Phys., <u>60</u>,3562(1974)

69. G.Herzberg, <u>Electronic spectra of polyatomic molecules</u> (Von Nostrand Publishing Co., New York (1966))

70. J.C.Stephenson and C.B. Moore, J.Chem.Phys., <u>52</u>, 2333(1970)

71. J.M. Prausnitz, <u>Molecular Thermodynamics of Fluid Phase Equilibria</u>, Prentice Hall, New Jersy (1969)

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